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THE CHEMICAL SOCIETY OF JAPAN.

Studies on the Molecular Structures of Some Cyanuric Compounds by Electron Diffraction

By Yûmi AKIMOTO*)

(Received April 13, 1954)

Recently, heterocyclic compounds have been studied theoretically from various points of view. We cannot admit, however, that we have so many experimental data available for this theory as for other spheres of study. In order to obtain such data, it may be necessary that more electron diffraction investigations be made on such heterocyclic compounds.

In this paper two kinds of cyanuric compounds, that is, cyanuric chloride and melamine are taken up. These compounds have a good symmetry, which makes it possible to measure the whole scheme of the molecules by comparatively few parameters. Therefore these compounds may be considered to be quite suitable for electron diffraction investigations.

Several crystalline cyanuric compounds have been investigated by the X-ray diffraction method[1-5]. We will mention here only the value given in Hughes' report of 1941 on melamine as it is directly related to this paper, which suggests that[1], $C\text{-}N_{ring}=1.33$–1.35 Å, $C\text{-}N_{outer}=1.35$–1.36 Å and $\angle N_r\text{-}C\text{-}N_r=123$–$125°$ within the error limit of about 0.02 Å. Reports concerning other cyanuric compounds will be quoted hereafter, when necessary.

Experimental

Each sample, cyanuric chloride (bp. 190°C) and melamine (sublimed over 300°C), was recrystallized before use. The electron diffraction photographs were made with these crystalline samples, which were vaporized into the apparatus previously described, with the help of a high temperature nozzle, newly designed for this purpose[7,8]. Gold foils were used for calibration of the electron wave length which was approximately 0.05–0.06 Å. The positions of halos were measured visually, and listed in Table I. The characteristic features of the photographs were represented by the visual curves $I_{vis}(q)$ and shown at the top of Fig. 3 and Fig. 5. From these curves, radial distribution curves were obtained by punched card summation of the formula

$$rD(r)=\sum_q I_{vis}(q)\exp(-aq^2)\sin(\pi qr/10)$$

with a chosen to give $\exp(-aq^2)=0.20$ at $q=80$.

The theoretical intensity curves

$$I(q)=\sum_i\sum_{i\neq j}(Z_iZ_j/r_{ij})\exp(-b_{ij}q^2)\sin(\pi qr_{ij}/10)$$

were calculated also for various models and compared with the visual curves.

TABLE I

THE OBSERVED q-VALUES FOR CYANURIC CHLORIDE AND MELAMINE

Max.	Min.	Cyanuric chloride	Melamine
1		17.2	18.6
2		(20.1)	(20.4)
	2	22.2	23.8
3		24.0	26.2
	3	26.1	28.1
4		28.0	31.1
	4	30.2	33.1
5		32.6	35.9
	5	36.0	
6		38.9	(39.2)
	6		41.9
7		(43.0)	45.6
	7	45.2	49.8
8		47.8	53.2
	8	52.9	57.4
9		55.3	62.0
10		(59.7)	
11		64.0	
12		70.2	
13		74.9	
14		78.9	

The values in the branckets were not used for quantitative comparisons.

Interpretation

In 1935, Knaggs[5] suggested that cyanuric triazide requires two unequal $C\text{-}N_r$ distances of 1.31 and 1.38 Å, corresponding essentially

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1) E.W. Hughes, *J. Am. Chem. Soc.*, **63**, 1737 (1941).
2) J.L. Hoard, ibid., **60**, 1194 (1938).
3) E.H. Wiebenga and N.F. Moremann, *Z. Krist.*, **99**, 217 (1938).
4) E.W. Hughes. *J. Chem. Phys.*, **3**, 1 (1935).
5) J.E. Knaggs, *Proc. Roy. Soc.* (London), **A150**, 576 (1935).
6) T. Yuzawa and M. Yamaha, This Bulletin, **26**, 414 (1953).
7) H. Oosaka and Y. Akimoto, ibid., **26**, 433 (1953).
8) L. Pauling and Sturdivant, *Proc. Nat. Acad. Sci.*, **23**, 615 (1937).

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to alternating double and single bonds. However, throughout all the X-ray diffraction investigation on various cyanuric compounds, this is the only work that suggested the inequality of cyanuric bonds. As the theoretical treatment of Pauling and Sturdivant[8] showed, such inequality seems very unusual, especially in the gaseous state. Moreover our result on the radial distribution curves does not support such a conclusion anyway. Therefore, in this work, we assumed the D_{3h} symmetry of the cyanuric ring: namely the equality of all cyanuric bonds. The same symmetry and co-planality were assumed throughout the whole molecular shapes[9]. Therefore, for cyanuric chloride only 3 parameters: C-N_r, C-Cl, and N_r-C-N_r, and for melamine 5 parameters: C-N_r, C-N_o, N_o-H, $\angle N_r$-C-N_r, and $\angle$H-N_o-H, are sufficient to determine the complete shapes of these molecules.

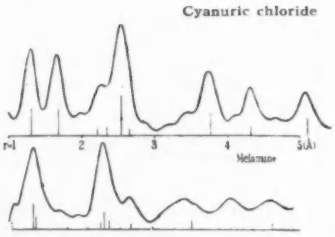

Fig. 1. Radial distribution curves for cyanuric chloride and melamine.

TABLE II
ASSUMED $<l^2_{ij}>^{1/2}_{AV}$ VALUES
($b_{ij}=(\pi^2/200)<l^2_{ij}>_{AV}$)

Cyanuric chloride		Melamine	
C-N_r	0.044	All C-N, N-N, and C-C	0
C-C′	0.053	distances	
N_r-N_r′	0.056	N_o-H	0.060
C-N_r″	0.061	All the other H-containing distances	0.083
C-Cl	0.045		
N_r-Cl′	0.057		
C-Cl″	0.072		
N_r-Cl‴	0.084		
Cl-Cl‴	0.095		

Cyanuric Chloride.—The radial distribution curve is shown at the upper part of Fig. 1. The following parameter set was the best obtained: C-N_r=1.33 Å, C-Cl=1.68 Å, and $\angle N_r$-C-N_r=125°.

The theoretical intensity curves were calculated for 32 models over the following parameter ranges: C-N_r=1.30–1.37 Å, C-Cl=1.60–1.70 Å, $\angle N_r$-C-N_r=115–130°, with b_{ij} values shown in Table II[10]. The q_{calc}/q_{obs} values and mean deviations of maxima and minima were calculated over all theoretical curves respectively. The relations of these values are picturized in Fig. 2 as a parameter chart which is essential for all models in the following parameter ranges: C-Cl=1.70–1.64 Å and $\angle N_r$-C-N_r=120–130°. C-N_r=1.33 Å, and N_r′-Cl=2.59 Å are the best values established from this chart. Several theoretical curves are shown in Fig. 3, and their parameters in Table III. Curve R has the best parameter set obtained from the radial distribution computation. Curves A–C were chosen to explain the differences of particular features from the visual curves. For such differences of features, a parameter chart was

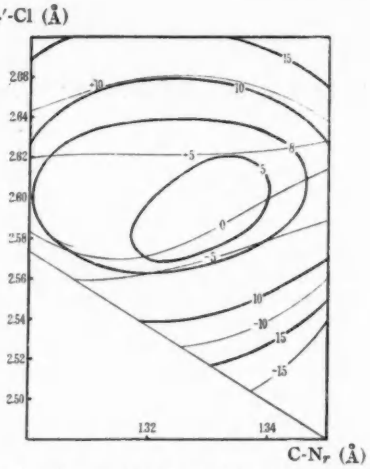

Fig. 2. Parameter chart of $q_{calc.}/q_{obs.}$ and mean deviations for cyanuric chloride.*
*Heavy lines are for $q_{calc.}/q_{obs.}$; and light curves for mean deviations. Numerical values must be multiplied by 10^{-3}.

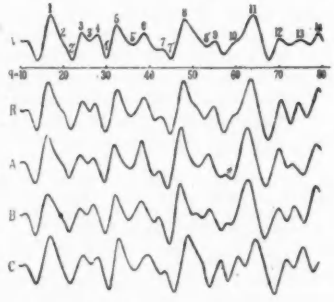

Fig. 3. Intensity curves for cyanuric chloride.

9) For melamine, several models, in which the planes through the N_o atom and the two H atoms are perpendicular with the ring plane, were also tested but with no sufficient changes of the curves.

10) In both cases, the curves are almost insensitive to slight changes of b_{ij} values.

TABLE III
MODELS FOR CYANURIC CHLORIDE

Model	C-N_r (Å)	C-Cl (Å)	$\angle N_r$-C-N_r
R	1.33	1.68	125°
A	1.32	1.70	120°
B	1.34	1.68	122.5°
C	1.34	1.66	130°

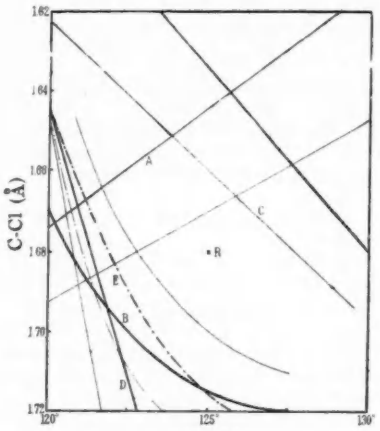

Fig. 4. Parameter chart of particular features for cyanuric chloride. Heavy lines indicate the border lines of models which have 1.34Å for C-N_r, and light lines 1.32Å for C-N_r.
Relative intensities of max. 3 and max. 4 (A), max. 5 and max.6 (B), and min. 8′ and 9′ (C), positions and shapes of max. 10 (D) and max. 13 (E) were quoted for the comparisons.

also made and shown in Fig. 4. Each line indicates where a particular feature of the intensity curves is sufficiently different from the visual curves to make them unacceptable.

Comparison of the two parameter charts leads us to the final set, C-N_r=1.33±0.02 Å, C-Cl=1.68±0.03 Å, and $\angle N_r$-C-N_r=125±3°. which is in complete agreement with the conclusion of the radial distribution argument.

Melamine.—The radial distribution curve is shown at the bottom of Fig. 1. The increase of the number of atoms makes the interpretation more difficult than that of the former. Overmore, the existence of hydrogen atoms makes almost all peaks considerably ambiguous. Therefore the direct determination of the 5 parameters is next to impossible. Assuming 120° for H-N_o-H and 1.04 Å for N_o-H, we can barely get to the following most possible parameter set: C-N_r= 1.34 Å, C-N_o=1.36–1.37 Å, and $\angle N_r$-C-N_r= 120–125°.

Twelve theoretical curves were calculated over the following ranges: C-N_r=1.32–1.38 Å, C-N_o=1.34–1.40 Å and $\angle N_r$-C-N_r=115–130°. N_o-H=1.04 Å and $\angle$H-N_o-H=120° were kept over all models. The b_{ij} values were taken as shown in Table II [10]. An effective value Z=1.25 was used for hydrogen atoms. Representative theoretical curves are shown in Fig. 5. The positions of several peaks are only sensitive for the change of the C-N_r distances. As these peaks are hardly affected by the change of the other parameters (for example, 0.02 Å changes of C-N_r distance is enough to shift Max. 5 by 1q, while 0.5 q shifts of the same peak requires the change

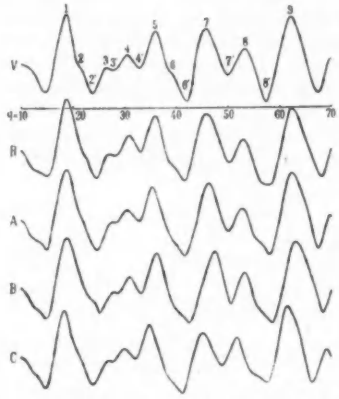

Fig. 5. Intensity curves for melamine.

TABLE IV
MODELS FOR MELAMINE

Model	C-N (Å)	C-N_o (Å)	$\angle N_r$-C-N_r
R	1.34	1.37	123°
A	1.34	1.36	120°
B	1.32	1.34	120°
C	1.36	1.36	120°

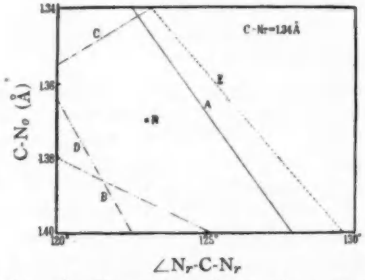

Fig. 6. Parameter chart of particular features for melamine.
Positions of max. 3 (A), max. 4 (B), max. 7 (C) and max. 8 (D), and existence of shelf between 8′ and 9 (E) were quoted for the comparisons.

of about 0.05 Å of C-N_o distance or 5° of $\angle N_r$-C-N_r), we can conclude safely that the C-N_r distance is 1.34±0.01 Å. To decide the other two parameters, the particular features are compared in Fig. 6 as a parameter chart.

Final conclusions are C-N_r=1.34±0.01 Å, C-N_o=1.37±0.03 Å and $\angle N_r$-C-N_r=123±3°.

Molecular Orbital Calculation

In order to discuss our results theoretically, simple MO calculations were applied to these compounds as well as to *sym*-trichlorobenzene and *sym*-triaminobenzene. The energy and wave function of each molecular orbital were obtained by the usual LCAO method. In the actual calculation, the exchange integral between non-adjacent atoms was neglected. Furthermore, for the Coulomb integral (α_r) and the exchange integral (β_{rs}) between two adjacent atoms, Sandorfy's values were employed, as shown in Table V[11]. Induction effect was assumed for α_r of the atoms which are next to hetero atoms to be 1/10.

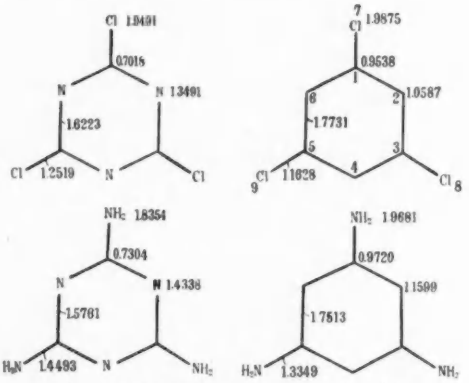

Fig. 7. Molecular diagrams by MO calculations.

By use of the molecular orbital wave function thus obtained, the electron density (q_r) and bond order (p_{rs}) were evaluated by the following equations:

$$q_r = 2\sum_n c^2_{rn}, \quad p_{rs} = 2\sum_n c_{rn}c_{sn}.$$

where C_{rn} is the coefficient of the r-th atomic wave function in the molecular orbital and the summation extends over the filled orbitals in the ground state. The results are shown in Fig 7.

TABLE V
SANDORFY'S INTEGRAL VALUES IN UNIT OF β[11]

Atom or bond	Integral value
C	4.10
N_r, N_o	5.17
Cl	5.08
C-C	1.00
C-N_r	1.22
C-N_o	0.80
C-Cl	0.39

Discussion

In Table VI, the results of the present investigations are compared with those of earlier works on the related compounds. About cyanuric chloride, the C-Cl distance (1.68 Å) is somewhat shorter than that of *sym*-trichlorobenzene (1.69 Å). On the C-N distance (1.33 Å), the same tendency is observed as compared with that of melamine (1.34 Å). We have not any accurate data to compare with the C-N_o distance (1.37 Å), but the inaccurate value (1.4 Å) for *p*-iodoaniline will serve to let us observe the similar tendency as the C-Cl distance of cyanuric chloride. Comparison of the bond order obtained above endorses these aspects.

11) M.C. Sandorfy., *Bull. chim. phys.*, **16**, 615 (1949).
12) L. O. Brockway and K. J. Palmer., *J. Am. Chem. Soc.*, **59**, 2181 (1937).
13) H. M. Powell, G. Huse and P. W. Cooke., *J. Chem. Soc.*, **1943**, 153

TABLE VI
COMPARISON OF PARAMETER VALUES ON THE RELATED COMPOUNDS (Å)

Molecule				method	reference
Cyanuric chloride	C-N=1.33±0.02,	C-Cl=1.68±0.03,	∠N-C-N=125±3°,.	E	
Melamine	C-N_r=1.34±0.01,	C-N_o=1.37±0.03,	$\angle N_r$-C-N_r=123±3°,.	E	
	C-N_r=1.33~1.35,	C-N_o=1.35~1.36,	$\angle N_r$-C-N_r=123~125°,.	X	1
Cyanuric acid	C-N_r=1.36,			X	3
Cyanuric triazide	C-N_r=1.33,	C-N_o=1.50,	$\angle N_r$-C-N_r=137°,.	X	4
	C-N_r=1.31,1.38,	C-N_o=1.38.		X	5
Trisodium tricyan melamine trihydrate	C-N_r=1.34,1,35,	C-N_o=1.40,.		X	2
sym-Trichlorobenzene	C-C=1.41(assum.),	C-Cl=1,69±0.03,.		E	11
m,*p*-Dichlorobenzene	C-C=1.40(assum.),	C-Cl=1.69±0.03,.		E	11
Chlorobenzene	C-C=1.39±0.02,	C-Cl=1.69±0.03,.		E	11
p-Iodoaniline	C-C=1.4,	C-N=1.4$_3$,.		X	12

E indicates the electron diffraction method and X the X-ray diffraction method.

In the case of benzene derivatives, C-C distance of the ring is almost independent of the number or the species of the substituent. On the other hand, the cyanuric ring seemingly cannot stand invariably against the change of circumstances. The certificate of this phenomenon can be obtained also from the MO treatment. The bond order of cyanuric C-N_r distance is more easily affected by the introduction of new π-electron systems than that of benzene C-C distance as shown in Fig. 7. The distortion of the cyanuric ring from the regular hexagon, may be understood as the effect of a lone pair which is located on each N_r atom.

Summary

1. The molecular structure of cyanuric chloride and melamine were investigated by the electron diffraction. The following values were obtained by the analysis based on D_{3h} symmetry of the molecules: C-N_r=1.33±0.02 Å, C-Cl=1.68±0.03 Å, and ∠N_r-C-N_r=125±3° for cyanuric chloride: C-N_r=1.34±0.01 Å, C-N_0=1.37±0.03 Å, and ∠N_r-C-N_r=123±3° for melamine assuming N_0-H=1.04 Å, ∠C-N_0-H=∠H-N_0-H=120°, and the coplanarity of all atoms.

2. Simple MO calculations were applied for both molecules as well as for *sym*-trichlorobenzene and *sym*-triaminobenzene. The resulted molecular diagrams were discussed together with the data obtained in the present experiment.

We are deeply indepted to Prof. A. Kotera and Assist. Prof. K. Suzuki for their continued encouragement and valuable advice for this study. The kindness of Dr. M. Uenaka who gave us the samples is gratefully acknowledged. Thanks are also due to Mr. M. Yamaha and Mr. M. Igarashi for their helpful discussion.

Chemical Laboratory, Tokyo Bunrika University, Tokyo

The Effect of Layered Water on the Color Reaction of Benzidine or Other Similar Compounds with Montmorillonite

By Hiroshi TAKAHASHI

(Received May 10, 1954)

Introduction

It is well known that certain clay minerals form stable complexes with some organic compounds. Complexes between montmorillonite and aromatic amines are particularly well known, because of their deep colors.[1,2] Investigations on the structure of the complexes as well as their color reactions have been reported by several authors. It has been clarified[3,4,5] through the X-ray diffraction method, that in these complexes organic molecules lie along can be held between two adjacent sheets of successive silicate layers, generally as a single layer or double layers just similar to the behavior of water molecules in natural montmorillonite. A schematic illustration of a montmorillonite complex after Hendricks and Jefferson[4,5] is shown in Fig. 1.

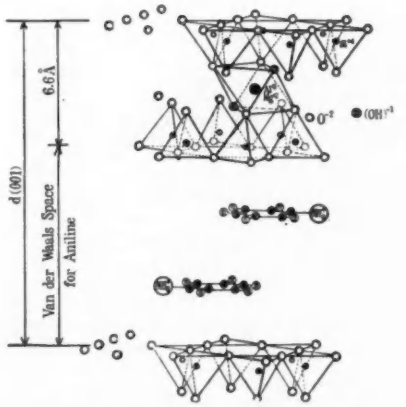

Fig. 1. Schematic drawing showing organic molecules between silicate layers of montmorillonite after Hendricks and Jefferson.

1) K. Kobayashi and K. Yamamoto, *J. Soc. Chem. Ind. Japan*, **26**, 289 (1921).
2) E.A. Hauser and M.B. Leggett, *J. Am. Chem. Soc.*, **62**, 1811 (1940).
3) J.B. Gieseking, *Soil Sci.*, **47**, 1 (1941).
4) S.B. Hendricks, *J. Phys. Chem.*, **45**, 65 (1941).
5) D.M.C. MacEwan, *Trans. Farad. Soc.*, **44**, 349 (1948).
6) S.B. Hendricks and M E. Jefferson, *Am. Mineral.*, **23**, 863 (1938).

In regard to the mechanism of the coloration displayed in the complex between montmorillonite and benzidine, Kameyama and Oka[7] have assumed that the benzidine molecule is colored in the semiquinone form due to the oxidation by the manganese ion which is present in clay as impurity, while, Weil-Malherbe and Weiss[8] ascribed it to the oxidation by the ferric ion present in the octahedral layer of the clay mineral. The present author, however, has found that the coloration is influenced remarkably by the amount of the absorbed water, i.e., interlayer water which is present between the adjacent silicate layers.[9,10] From this point of view, the present article will report on the mechanism of the formation of complexes as well as the color reactions between some montmorillonite and benzidine or some related compounds, discussing them in comparison with each other.

Clay Samples.—The clays used in this experiment are Wyoming bentonite, Bodai acid clay and Numata clay, from Osage, Wyoming, U.S.A., Bodai, Naya-mura, Ishikawa Prefecture and Shimokawada, Kawada-mura, Gunma Prefecture, respectively. The refined samples have been obtained from these clays after having thoroughly elutriated them in the usual way. The X-ray powder patterns of these samples have shown that they have montmorillonite for the main ingredient.[11] Bodai acid clay alone, however, contains α-cristobalite and quartz as impurities. (Cf. Table I)

Their differential thermal analysis curves (Fig. 2) reveal that they are montmorillonite type, and the rate of heating is 12°C per minute.[12] In this figure, however, Numata clay alone has an endothermic peak at 560°C, which may be due to the possible presence of illite or kaolin minerals as an impurity in Numata clay,[13] though its presence has not yet been found in the X-ray powder pattern.

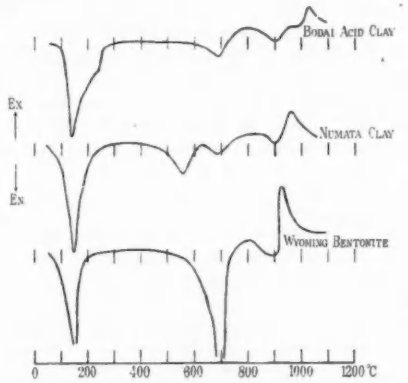

Fig. 2. Differential thermal analysis curves of clay samples.

The chemical formulas[14,15] obtained from the chemical analysis of these clay samples, all of which are assumed as montmorillonite, are given below:

Wyoming bentonite:

$$(Al_{1.50}Fe_{.18}Mg_{.32})\ (Al_{.01}Si_{3.99})O_{10}(OH)_2X^{I}_{.33}$$

Bodai acid clay:

TABLE I

THE X-RAY POWDER PATTERNS OF CLAY SAMPLES

Indices	Bodai acid clay		Numata clay		Wyoming bentonite	
	d	*I*	*d*	*I*	*d*	*I*
001	15.4	10	15.4	10	15.4	10
003	5.14	2	5.15	1	5.16	1
02,11	4.46	6	4.50	5	4.51	5
	4.21 (Q)					
	4.04 (α-C)					
	3.35 (Q)					
005	3.09	2	3.05	1	3.07	2
13,20	2.56	3	2.57	2	2.58	2
31,15,24	1.72	0.5	1.69	0.5	1.70	0.5
33,06	1.498	3	1.496	2	1.500	3

Key to abbreviations: d=spacing in kx, I=intensity, Q=quartz pattern, α−C=α−cristobalite pattern

7) N. Kameyama and S. Oka, *J. Soc. Chem. Ind. Japan*, **32**, 294 (1929).
8) H. Weil-Malherbe and J. Weiss, *J. Chem. Soc.*, **1948**, 2164.
9) S.B. Hendricks, R.A. Nelson and L.T. Alexander, *J. Am. Chem. Soc.*, **62**, 1457 (1940).
10) J. Mering, *Trans. Farad. Soc.*, **42-B**, 205 (1946).
11) D.M.C. MacEwan, "X-ray Identification and Crystal Structures of Clay Minerals", edited by G.W. Brindley, The Mineralogical Society (Clay Mineral Group). London, (1951) p. 124.
12) R.E. Grim, "Clay Mineralogy", McGraw-Hill Book Co., Inc., New York, N.Y., (1953), p. 197.
13) T. Sudo et al., *J. Geol. Soc. Japan*, **58**, 115 (1952).
14) C.S. Ross and S.B. Hendricks, *U.S. Geol. Surv. Bull.*, Prof. Paper, **205-B**, 23 (1945).
15) Y. Otsubo, "Chemical Researches, No. 8", Asakura Book Co., Tokyo, (1950), p. 85.

$(Al_{1.64}Fe._{15}Mg._{32})\ (Al._{13}Si_{3.87})O_{10}(OH)_2X^I._{34}$

Numata clay:

$(Al_{1.55}Fe._{16}Mg._{33})\ (Al._{08}Si_{3.92})O_{10}(OH)_2X^I._{29}$

Exchangeable cation is sodium in Wyoming bentonite and Numata clay, while it may be both sodium and calcium in Bodai acid clay. However, as it may be considered to have the least effect on the color reaction of complexes, further discussion on cation exchange seems to be unnecessary for the present purpose.

Of the plate type and fluffy type which usually characterize the shape of montmorillonite, these clays are considered to belong to the latter type, from the electron micrographs of them.[16,17,18]

As a result of all the experiments above, it seems to be certain that these clay samples are montmorillonite.

Preparation of Specimens.—Complexes between montmorillonite and every one of the following organic substances such as benzidine, γ-diphenol, aniline, phenol, *p*-phenylenediamine and monomethyl-*p*-aminophenol were prepared for the present investigation. To prepare a complex, the water-alcohol solution of a given organic compound is poured into an aqueous suspension of clay. The amount of the organic compound which is added is as much as several times the base exchange capacity of the clay (5–10 milliequivalent per one gram of clay). The suspension of the complex thus prepared was centrifuged after left over twenty four hours. The precipitates obtained were washed with alcohol and water repeatedly until free compounds were no longer present, and dried in air. From every kind of these air dried complexes, four kinds of specimens were made by the following processes:

(1) Absorption of water by standing in the saturated water vapor at 20°C for about a week,

(2) complete absorption of water by direct wetting,

(3) dehydration by standing over phosphorus pentoxide,

(4) absorption of water by wetting again after (3) procedure was applied.

The specimens prepared by these processes will hereinafter be abbreviated as S-1, S-2, S-3 and S-4 for every complex.

Experimental and Discussion

It was found that the color of the complex is varied remarkably, in some cases, accordingly to the way of preparation of the specimen, and in other cases, it is not. The colors of specimens of each complex are shown in Table II, along with the values of their (001) spacings obtained by a Philips X-ray Geiger counter spectrometer. Filtered copper radiation, 35 Kv, 15 Ma, scan speeds 2° and 1/2° per minute, angular aperture 1°, receiving slit 0.006 inch, time constant 4 second.

Table II

The (001) spacings and the colors of the specimens for each complex

		Bodai acid clay	Numata clay	Wyoming bentonite	color
benzidine	S-1	15.4 kx	15.4	15.3	blue
	S-2	19	19	19	blue
	S-3	13.8	13.9	13.2	yellow∼colorless
	S-4	19	19	19	blue
γ-diphenol	S-1	16.1			green
	S-2	19.5			green
	S-3	14.7			colorless
	S-4	19.5			green
aniline	S-1	15.3	15.2	15.2	very light violet
	S-2	18	18	19	very light violet
	S-3	13.5	13.5	12·4	very light violet∼colorless
	S-4	18	18	19	very light violet
phenol	S-1	15.2	15.2	15.2	colorless
	S-2	18	19	18.5	colorless
	S-3	14.5	14.5	13.4	colorless
	S-4	19	18	18.5	colorless
p-phenylene diamine	S-1	15.4	15.4	15.4	violet (blue)
	S-2	15.4	15.4	15.4	violet
	S-3	15.2	14.5	14.7	violet
	S-4	15.4	15.4	15.4	violet
mono-methyl -*p*-amino phenol	S-1	15.4	15.3	15.3	violet (light green)
	S-2	15.4	15.3	15.4	violet
	S-3	15.1	13.3	14.0	violet
	S-4	15.4	15.2	15.4	violet

With respect to the benzidine complex, Table II reveals that the color reaction is caused by the presence of water and when dehydrated as S-3 the color can not be developed. The color of the air dried complex when it is further dried over calcium chloride becomes yellowish green and the (001) spacing is 14.5–15.0 kx. The yellowish green color gradually turns to blue when the complex is in equilibrium with water vapor, and

16) R.P. Humbert and B.T. Shaw, *Soil Sci.*, 52, 481 (1941).

17) B.T. Shaw, *J. Phys. Chem.*, 46, 1032 (1942).

18) P.F. Kerr et al., "API Report Project 49", No. 6 (1950).

TABLE III
THE VARIATION OF (001) SPACINGS OF CLAYS AND THEIR BENZIDINE COMPLEXES WITH THE ABSORPTION OF WATER

	Bodai acid clay		Numata clay		Wyoming bentonite	
	natural clay	complex	natural clay	complex	natural clay	complex
absorbed water vapor	15.4 kx	15.4	15.4	15.4	15.4	15.3
saturated with water	19	19	19	19		19
dried over $CaCl_2$	13.6	14.8	13.7	14.9	13.3	14.5
dried over P_2O_5	12.4	13.8	12.4	13.9	12.0	13.2

the (001) spacing becomes equal to the value of S-1. It is inferred from this fact that, in the case of the benzidine complex, the color varies, depending on the amount of water held between two neighbouring sheets of successive silicate layers.

Table III shows the variation of the (001) spacings of the clay samples with the absorption of water, in comparison with their benzidine complexes. The (001) spacing of natural clays are 15.4 kx when they are in equilibrium with water vapor. This implies that they have two water layers between two adjacent silicate layers. When the clays are saturated with water, they swell and in the case of Bodai acid clay and Numata clay, the (001) spacing increases to 19 kx, which corresponds to the increment of one or two water layers, whereas, in Wyoming bentonite, the (001) spacing becomes too large to estimate its value. When benzidine complex is saturated with water, the increment in the number of water layers is one or two, just as in the case of natural Bodai and Numata clay. As well as in the case of Wyoming bentonite; it is of interest to note that it can not swell so much as in the natural state when it forms a complex.

Table III shows also that even in the dehydrated state there still remain the benzidine molecules themselves between the silicate layers. Therefore, decoloration is caused, not by the absence of benzidine molecules themselves, but by the absence of water.

The presence of the layered water is necessary for the color reaction; moreover, it was found that some liquids other than water also show the same effect. For the purpose of estimating the absorbed water thoroughly, the clay was heated to 300–400°C. That the layered water is no longer present in it, is demonstrated by its X-ray diffraction diagram, by which, its (001) spacing was found to be 9.5 kx. When a water solution, an alcohol solution and an acetone solution of benzidine were added to the dehydrated clay respectively, it was found that the color of the complex became blue, greenish blue and yellow according to the solvent. This fact means that the color reaction of this complex changes according to the kind of liquid which is present between layers.

The same effect is also demonstrated in the following way. When water, alcohol and acetone are added respectively to a benzidine complex which has been dehydrated thoroughly to a colorless state, it becomes blue, greenish blue and yellow respectively as above. In this case, however, if benzene is added to the complex, the appearence of color can not be observed.

r-diphenol whose construction approximates to benzidine, shows similar behavior in the formation of complex with these clays. However, amino-radical has a greater effect of deepening the color of the complex than in the case of hydroxyl-radical as revealed from Table II.

p-Phenylenediamine(paramine)-montmorillonite and monomethyl-*p*-aminophenol(methol)-montmorillonite complexes have deep colors, which do not change even when they are dried, in contrast with the case of benzidine or *r*-diphenol complex. It is worthy to note that there is no difference in the value of (001) spacing between S-2 and S-3 (the dried state and the water saturated state). It is presumably because of the fact that these complexes in themselves have little layered water, and even when they are dried or saturated with water, it dose not affect the quantity of the layered water in them. What deserves particular attention here is the fact that, in the paramine and methol complexes, their colors are blue and green respectively when they are made freshly in the clay suspension, and then these colors change to violet as time passes or if they are dehydrated. This fact may lead to an assumption that in the first stage of the formation, these complexes temporarily make benzidine-like coloration, but in the next stage their colors change as the molecules of paramine or methol fix on both sides of the silicate layers, no longer permitting the water molecules to get into them. It is, however, ascertained through X-rays that in the case where the quantity of paramine and of methol is not saturated, the shrinkage or swelling occurs to some extent of movement of the water getting into or out of them.

In contrast with paramine and methol, the coloration of the aniline complex is not so remarkable. In the case of phenol, which is believed to be able to form a complex with montmorillonite,[2,5] the coloration can not be recognized by the naked eye. This unremarkable coloration is due to the fact that aniline and phenol are monofunctional compounds, and the amino- or hydroxyl-radical

fixes on one side of the silicate layer. When these complexes are saturated with water, the increment in the number of water layers is one or two just as in the case of benzidine complex.

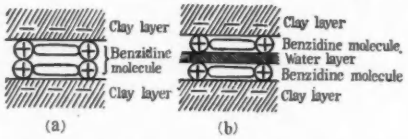

Fig 3. The process of benzidine complex formation with montmorillonite.
(a) Complex is formed.
(b) Saturated with water.

The benzidine and paramine complexes show a remarkable coloration, as they are bifunctional compounds. In the case of the benzidine complex, a benzidine molecule fixes on one side of the silicate layer, and then when it is saturated with water, the water molecules get into the silicate layer. From this fact, a schematic drawing of the process of benzidine complex formation with montmorillonite is shown in Fig. 3.

Summary

The relationship between layered water and coloration of some complexes between montmorillonite and benzidine or other similar compounds has been discussed, and it is shown that they may be divided into types according to the structures of organic compounds. The shrinkage and swelling of the layer distance of the complex caused by its dehydration and hydration are observed.

The coloration of the monofunctional-complex is not so remarkable and that of the bifunctional-complex is remarkable. In the case of monofunctional-complex or the bifunctional-complex with benzidine, the amino- or hydroxyl-radical fixes on one side of the silicate layer, and then, when it is saturated with water, the water molecules get into the silicate layer. On the other hand, in the bifunctional-complex with paramine, as the amino- or hydroxyl-radical fixes on both sides of the silicate layers, the water molecules no longer get into it.

The author wishes to express his hearty thanks to Prof. H. Akamatu for his kind guidance and encouragement.

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Surface Chemistry of Synthetic Protein Analogues. V. On the Effect of Salt on the Monolayers of the Copolypeptide of L-Lysine, L-Phenylalanine and L-Glutamic Acid

By Kozo HAMAGUCHI and Toshizo ISEMURA

(Received May 22, 1954)

Introduction

In the previous paper,[1] we have reported on the behaviour of the monolayers of the electrolytic polypeptides, poly-L-glutamic acid and a copolypeptide of L-lysine, L-leucine and L-glutamic acid, in relation to the pH's of substrates. In the present paper, we shall report on the effect of salts on the monolayers of the copolypeptide of L-lysine, L-phenylalanine and L-glutamic acid. The interaction between natural proteins and salts is important in biological systems. The numerous investigations on these interactions have been carried out in bulk solution,[2] but few in interfaces.[3,4] In the recent investigations of protein by spreading monolayer, concentrated solutions of salts such as ammonium sulphate, are generally used as substrates in order to prevent the proteins from passing into substrate water.[5] Since there exist also some interactions between protein and salts at interface, a detailed knowledge of the interaction between protein molecules and salts in the substrate is indispensable for a thorough understanding of the behaviour of protein monolayers on salt solution.

For these reasons we have examined the effect of salt, i.e., potassium chloride, on the

1) T. Isemura and K. Hamaguchi, This Bulletin, **27**, 339 (1954).

2) F. Haurowitz, "Chemistry and Biology of Proteins," pp. 66 (1950).

3) A. Lajtha and E. K. Rideal, *Arch. Biochem. Biophys.*, **33**, 252 (1951).

4) E. Fredericq, *Biochim. et Biophys. Acta*, **9**, 601 (1952).

5) H. B. Bull, *J. Am. Chem. Soc.*, **67**, 4, 8, (1945).

monolayers of the amphoteric polypeptide which appears very promising as a protein model.

Experimental

Material and Methods.—The copolypeptide of L-lysine, L-phenylalnine and L-glutamic acid was prepared by Dr. H. Tani and Mr. H. Yuki[6] and was used without any further purification. This copolypeptide was spread from a solution in N/100 hydrochloric acid to which 10 per cent of isopropyl alcohol was added. Surface pressure and surface viscosity measurements were carried out by the method of hanging plate and of damped oscillatory motion of disc, as reported in the previous papers.[7,8] Potassium chloride was recrystallized three times from water. The pH's of the substrates were adjusted by hydrochloric acid for lower pH values and by potassium bicarbonate or potassium carbonate for higher pH's, which were used by Langmuir and Shaefer for the studies of the effect of salts on the fatty acid monolayers.[9] The areas per amino-acid residue of the copolypeptide were calculated by assuming that the same ratio of L-lysine, L-phenylalanine and L-glutamic acid as the initial monomer concentration, 1:3:1, was maintained in the copolymer. This assumption turned out to be probably true throughout the analysis of the results.

Results.—The copolypeptide of L-lysine, L-phenylalanine and L-glutamic acid was soluble in the substrates which did not contain any salts. The stable monolayers were obtained when aqueous solutions of potassium chloride were used as substrates. To find out the concentration of potassium chloride, in the substrate solution necessary for giving a stable monolayer, the areas at constant surface pressure (1 dyne/cm.) against the concentration of potassium chloride are plotted as in Fig. 1. From this figure, one per cent of potassium chloride in the substrate was found to be sufficient to obtain a stable monolayer.

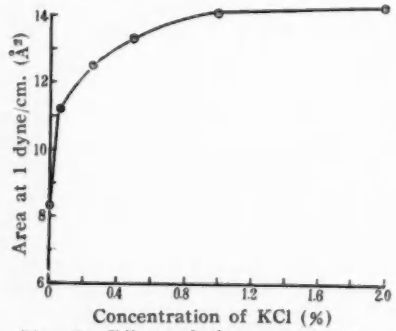

Fig. 1. Effect of the concentration of potassium chloride on the area per residue at 1 dyne/cm (pH 5.6).

6) H. Tani, H. Yuki, K. Okawa, S. Sakakibara and C. Oizumi, *Sen-i Kagaku Kenkyusho Nempo* (*Mem. Inst. Fiber Research*), 7, 98 (1953).

7) T. Isemura and K. Hamaguchi, This Bulletin, 25, 40 (1952).

8) T. Isemura and K. Hamaguchi, ibid., 27, 125 (1954).

9) I. Langmuir and V. J. Shaefer, *J. Am. Chem. Soc.*, 59, 2400 (1937).

The variations of the surface pressure-area (F-A) curves with the pH's of the substrates of constant KCl concentration (0.07 mole/litre), are shown in Fig. 2.

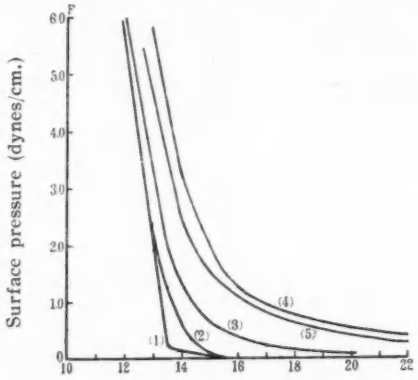

Fig. 2. Variations of F-A curves with the pH's of substrates; (1) pH 5.6—8.0, (2) pH 5.0, (3) pH 3.8, (4) pH 2.2, (5) pH 10.3 (0.07 mol. of KCl/litre).

A single F-A curve of condensed type was obtained in the pH range between 5.6 and 8.0. Changing the pH values of the substrate out of this pH range, F-A curves expanded gradually. The areas per residue at 1 dyne/cm. against pH's of the substrates are plotted in Fig. 3.

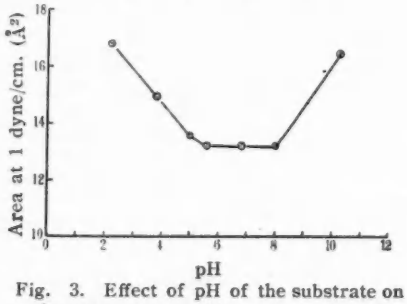

Fig. 3. Effect of pH of the substrate on the area per residue at 1 dyne/cm. (0.07 M KCl).

In this figure the minimum area region which is parallel to the pH axis, appears between pH 5.6 and 8.0.

The variations of F-A curves as the function of the concentration of potassium chloride in the substrate at constant pH (pH 2.2) are shown in Fig. 4.

It would be clear from this figure that the film expands with the decrease in the concentration of potassium chloride.

The surface viscosity-area (η-A) curves of the copolypeptide on the substrates of different concentrations of potassium chloride (at pH 5.6) are shown in Fig. 5. Fig. 6 shows the curve of η at constant area (at 17 Å²/residue) plotted against the concentration of potassium chloride.

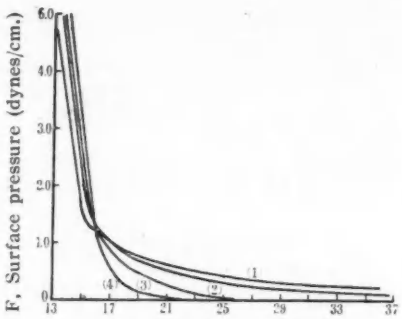

Fig. 4. Variations of F-A curves with concentration of KCl. (1) 0.035 M, (2) 0.07 M, (3) 0.13 M, (4) 0.40 M KCl. (pH 2.2)

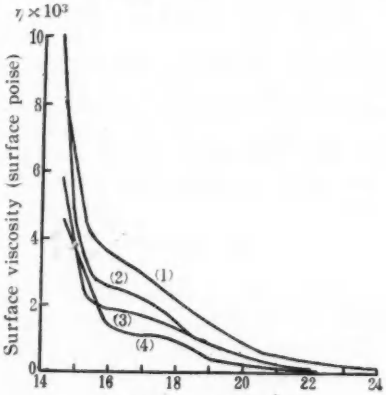

Fig. 5. Effect of KCl on the η-A curves of the copolypeptide. (1) 0.07 M, (2) 0.14 M, (3) 0.28 M, (4) 0.56 M KCl. (pH 5.6)

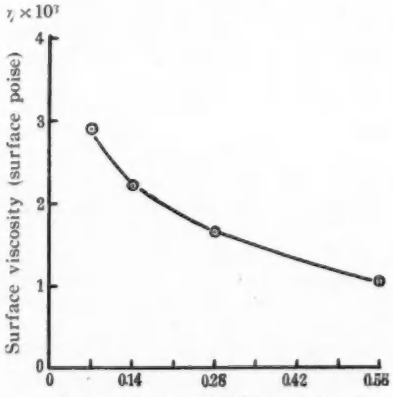

Fig. 6. Effect of the concentration of KCl on the surface viscosity (at 17Å²/residue). (pH 5.6)

The greater the concentration of potassium chloride becomes, the lower is the surface viscosity at constant area. Thus, the effect of potassium chloride on the η-A curves could be detected markedly while no effect on the F-A curves was observed when more than 1% potassium chloride was present in the substrates (Fig. 1). The fact recognized in common with all these η-A curves was that the surface viscosity begins to increase steeply at the area of 15.9 Å²/residue, irrespective of the concentration of potassium chloride.

The η-A curves of the copolypeptide on the substrates of different pH values, maintaining the concentration of KCl to be constant (0.28 M/litre), are shown in Fig. 7. Fig. 8 shows the surface viscosities at constant area (17 Å²/residue) against pH curve.

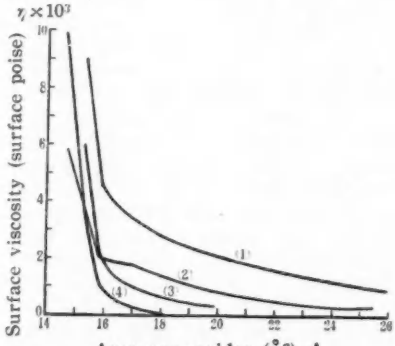

Fig. 7. Effect of pH on η-A curves of the copolypeptide (1) pH 6.8, (2) pH 5.6, (3) pH 8.0, (4) pH 2.2 (0.28 M KCl).

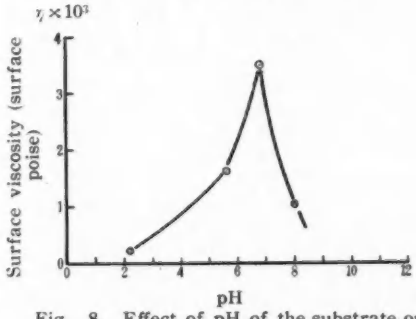

Fig. 8. Effect of pH of the substrate on surface viscosity (at 17Å²/residue). (0.28 M KCl)

It has been found from these figures that the surface viscosity becomes maximum at pH 6.8. On a more acidic substrate, the value of surface viscosity rather fluctuated and reproducible η-A curves could not be obtained in the pH range between 5.0 and 3.8.

Discussion

The Relationships between F-A Curves and pH's of Substrates (at Constant Con-

centration of KCl).—As shown in Fig. 2, the monolayers of the copolypeptide at pH between 5.6 and 8.0 of the substrates gave the same F-A curve of condensed type and in both the outsides of this pH range the F-A curves were of expanded type. The minimum area region appearing in the area (at constant pressure) against pH's of substrates curve (Fig. 3), corresponds to the region in which F-A curves have condensed type. This region between pH 5.6 and 8.0 corresponds to the isoelectric region and would be designated as the "isoelectric band" of the copolypeptide at this salt concentration (0.07 M/litre). When salts are contained in the substrate the isoelectric "band" appears rather than a "point" and the width of this band is the function of the salt concentration; an increase in the concentration of salt in the substrate widened the band. Even at pH 2.2, therefore, the F-A curves were of condensed type and it was expected that the F-A curves would represent the isoelectric property throughout all the pH's of the substrates, if potassium chloride was present in the concentration of more than 0.42 M/litre. This is due to the effect that an increase in ionic strength would reduce the coulombic force between the ionized groups of the copolypeptide. The fact that the film expands at each side outer than the isoelectric region is due to the electrostatic repulsion of $-COO^-$ or $-NH_3^+$ ions themselves when the one group exceeds the other.

In the previous paper,[1] it was pointed out that in the case of the copolypeptide of L-lysine, L-leucine and L-glutamic acid, the area at constant pressure against pH curve is of W-shape in the absence of salts in the substrate and that this fact can be interpreted in terms of free charge ($\Delta\alpha=|\alpha_L-\alpha_G|$) and of salt linkage ($\alpha_L\cdot\alpha_G$), if α_L and α_G represent the ionization degree of amino and carboxyl groups. Referring to the present results, salts would have the effect of depressing the maximum point appearing in the $(A)_F$-pH curve. Detailed considerations about this effect will be present in the later part of this paper.

The Relationships between F-A Curves and Ionic Strength of Substrates (at Constant pH).—The effect of potassium chloride on the F-A curves of this copolypeptide is shown in Fig. 4. It may be found from this figure that the films are more expanded at low ionic strength in the substrates. This fact can be interpreted by the increment of the surface pressure due to the free energy of the electrical double layer which is formed between the ionized groups of the monolayer (in this case, $-NH_3^+$ ions of lysine residues) and the counter ions (Cl^-).

We can calculate the electrical potential difference of the double layer underneath the film from the F-A curves by the procedure adopted by J. T. Davies.[10,11]

According to Verwey and Overbeek,[12] the free energy of the double layer is represented by

$$G_s=-\frac{8nkT}{\kappa}\left(\cosh\frac{ze\psi_0}{2kT}-1\right), \qquad (1)$$

where k is the Boltzmann constant, T the absolute temperature, n the number of ions in 1 cc. of bulk solution, i.e., $n=NC/1000$ (C: mol./litre, N: Avogadro number), z the valency of salt, e the electronic charge, ψ_0 the surface potential and $\kappa=\sqrt{\frac{8\pi nz^2e^2}{\varepsilon kT}}$ (ε: dielectric constant).

The surface tension is equivalent to the surface free energy per unit area. When the electrical double layer is formed, the surface tension is decreased by G_s (because of the negative sign of equation (1)) and correspondingly the surface pressure is increased by ΔF, namely

$$\Delta F=-G_s=\frac{8nkT}{\kappa}\left(\cosh\frac{ze\psi_0}{2kT}-1\right). \qquad (2)$$

After numerical substitution with $k=1.38\times10^{-16}$ erg/°K, $T=293$°K, $\varepsilon=80$, $e=4.8\times10^{-10}$ e.s.u., $z=1$, the following relation is obtained:

$$\Delta F=6.1\sqrt{c}\left(\cosh\frac{ze\psi_0}{2kT}-1\right). \qquad (3)$$

From Eq. (3)

$$\psi_0=51.2\ \cosh^{-1}\left(1+\frac{\Delta F}{6.1\sqrt{c}}\right) \qquad (4)$$

is obtained, where ψ_0 is expressed in millivolt units.

The surface pressure increment (ΔF) due to the presence of the electrical double layer is written

$$\Delta F=F^+-F^\circ, \qquad (5)$$

where F^+ is the observed pressure and F° the pressure if the film had no charged groups. F° is a negative quantity, as shown in the later part, so it might be recognized as the cohesional force between film molecules.

On the other hand, the Gouy potential ψ_G, which is at a uniformly charged surface when uni-univalent salts are present, is expressed as

10) J. T. Davies, *Proc. Roy. Soc.*, A208, 224 (1951).
11) K. Hamaguchi, *Mem. Inst. Sci. Ind. Res., Osaka University*, **11**, 175 (1954).
12) H. R. Kruyt, "Colloid Science," Elsevier, Vol. I, pp. 140 (1952).

$$\psi_G = 2.303\frac{kT}{e}\log\left(\frac{134^2\times 4}{A^2C}\right), \qquad (6)$$

where A is the area per ion of film-forming substance in Å² unit.

If we assume that ψ_G is the same as ψ_0, we can calculate ψ_0 by Eq. (6). However, the following two assumptions are necessary: (a) At pH 2.2 all the $-NH_2$ groups of lysine residues are ionized to $-NH_2^+$ ions. (b) It is difficult to find out the area per ion in the case of polyampholytes. In the present case, we assume in regard to the first approximation as described above, that the initial monomer concentration ratio of lysine, phenylalanine and glutamic acid residues, i.e., 1:3:1, is maintained in the copolymer produced, so that the area per $-NH_3^+$ ion may be five times the area per residue. By these assumptions ψ_0 can be calculated by Eq. (6) for the case of 20 Å²/residue, namely 100 Å²/$-NH_3^+$ ion. ψ_0 becomes 115 mv. when c=0.075 mol./litre. Substituting this figure in Eq. (4) and then in Eq. (5) we obtain $F^\circ = -5.8$ dynes/cm. Using this F° value ψ_0 can be calculated by Eq. (4) at different salt concentrations. The results are summarized in Table I.

TABLE I

c (mol./litre)	F (dynes/cm.) at 20 Å²/residue	ψ_0 (mv.) calculated from eq. (4)	ψ_0 (mv.) calculated from eq. (6)
0.04	0.65	130	131
0.075	0.55	115	115
0.135	0.30	102	100
0.405	0.05	80.4	72.8

The values of ψ_0 calculated from Eq. (4) are in close agreement with those of ψ_G from (6). Therefore, the following equation, which is readily derived from Eq. (6), is also applied for ψ_0 values calculated from the F–A curves.

$$\left(\frac{\partial\psi_0}{\partial\log\sigma}\right)_A = -59\ mv. \qquad (7)$$

This relation was found for the monolayers of α-brompalmitic acid[13] and of octadecyltrimethylammonium chloride[10] on the substrates containing sodium chloride.

The Relationships between η-A Curves and Ionic Strength or pH's of Substrates.— As shown in Figs. 5 and 6 an increase of the ionic strength in the substrate accompanied the decrease of the surface viscosity and the surface viscosity began to increase steeply at the area of about 15.9 Å²/residue. This area corresponds to the area per residue calculated with the X-ray data for close packed arrangement of peptide of β-configuration.[7]

Cumper and Alexander[14,15] showed that although the effect of the ionic strength of salts could not be detected for the spreading monolayers of proteins, in the case of adsorbed protein films an increase in ionic strength decreased the surface viscosities. We could find out the same effect for the spreading monolayers of the copolypeptide as for the adsorbed films found by them.

There are two possibilities to explain why the surface viscosity decreased by an increase in ionic strength of salts in the substrate.

(a) In the case of polyelectrolyte solutions, the viscosity is generally decreased by an increase in salt concentration, and this might attributed to the coiling of polyelectrolyte molecules, for salt reduces the electrostatic repulsion between the intramolecular charged groups.[15] The relation between the surface viscosities and the salt concentration which was found in the present experiments (Fig. 6), is analogous to the bulk viscometric behaviour of polyelectrolytes just mentioned. The surface viscometric behaviour would be, therefore, explained by the same reason as for bulk viscosities.

(b) There exist many salt-linkages between $-NH_3^+$ and $-COO^-$ ions at pH 5.6, for this pH value lies in the isoelectric band as described previously. The high surface viscosities would be the result of the great resistance due to these inter- or intramolecular salt-linkages. By the presence of salts, however, the coulombic force between $-NH_3^+$ and $-COO^-$ ions is minimized. Therefore, the effect of salt on the surface viscosities would be interpreted in terms of this reducing effect of electrostatic interaction.

The former possibility (a) cannot be admitted for the following reasons. The areas where the effect of salts appears, are smaller than 21 Å²/residue and this smaller area region corresponds to the state in which polymer molecules are very close to each other. In such a state it could not be considered that the surface viscosity depends on the shape of each polymer molecule. Furthermore, if the increase in surface viscosity by the decrease in the concentration of salt would be due to the elongation of a polymer molecule, the reason why a maximum point appears in the $(\eta)_A$– pH curve (Fig. 8), cannot be ex-

13) D. J. Crisp, Surface Chemistry (*Research Supplement*), Butterworth, (1949) p. 65.

14) C. W. N. Cumper and A. E. Alexander, *Trans. Faraday Soc.*, **46**, 235 (1950).

15) C. W. N. Cumper and A. E. Alexander, *Revs. Pure and Applied Chem.* (Australia), **1**, 121 (1951).

16) A. Katchalsky, *J. Polymer Sci.*, **7**, 393 (1951).

plained. These facts support the possibility (b). Davies,[17] in his paper on the shape of protein molecules at interfaces, considered that the surface viscosity of protein at oil-water interface is very much higher than at air-water interface, is one of the evidences that the protein molecules are to a greater extent unfolded into long chains of considerable flexibility at the former than at the latter. He compared, however, the surface viscosity at oil-water interface with that at air-water interface in a region of very small area. Furthermore, he referred to Joly's data[18] of surface viscosities at air-water interface in which the substrate was acidified by N/100 HCl and also to the data of Cumper and Alexander[14] at oil-water interface in which the pH's of the aqueous phase were not described explicitly. However, in view of our results mentioned above, we cannot agree with his opinion. Inokuchi[19] pointed out that the area at which the instantaneous elasticity of egg albumin films appears on 5% ammonium sulphate solution at pH 5.5, was three times the area as on 0.1 N HCl. This would also be interpreted in terms of salt-linkages when we take into account that the isoelectric point of the protein lies at pH 4.8.

The decrease in surface viscosities at constant area is approximately proportional to the square root of the ionic strength in the substrate. This fact corresponds to the bulk viscosity or rigidity of very concentrated gelatin solutions.

The Relationships between $(A)_F$-pH, $(\eta)_A$-pH, $\Delta\alpha$-pH and $\alpha_L \cdot \alpha_G$-pH Curves.—In the previous paper,[1] it was pointed out that the $(A)_{For\eta}$ (at constant F or at constant η)-pH curve which was obtained with the films of the copolypeptide of L-lysine, L-leucine and L-glutamic acid on the substrate which did not contain any salts, was of W-shape and the maximum point in this curve corresponded to its isoelectric point. We calculated the ionization degrees of $-NH_2$ groups of lysine residue (α_L) and of -COOH groups of glutamic acid residue (α_G) at each pH by the following simple approximate equation

$$pH - pK_0 = \log \frac{\alpha}{1-\alpha}, \qquad (8)$$

where K_0 is the intrinsic dissociation constant which is assumed to be 10.5 and 4.3 for $-NH_2$ and -COOH groups, respectively. $\Delta\alpha = |\alpha_L - \alpha_G|$ might be assumed to give a measure of effective free charges and $\alpha_L \cdot \alpha_G$ the probability of salt-linkages. This assumption might be justified if the polymerization ratio of lysine and glutamic acid is 1:1. The W-shaped $(A)_{For\eta}$-pH curve could be interpreted as follows in terms of the $\Delta\alpha$-pH and $\alpha_L \cdot \alpha_G$-pH curves. $\alpha_L \cdot \alpha_G$-pH curve showed a maximum at pH 7.0 and the $(A)_{For\eta}$-pH curve also showed a maximum at this pH. When the substrate becomes more acidic or alkaline from this isoelectric point, the area becomes smaller and this region corresponds to the droop $\alpha_L \cdot \alpha_G$-pH curve. In this region the effect of $\alpha_L \cdot \alpha_G$ is more predominant than that of $\Delta\alpha$, i.e., the effect of salt-linkages is more pronounced than that of electrical repulsion by free charges. When the substrate becomes still more acidic or alkaline, the area becomes larger again and these regions correspond to the rise of the $\Delta\alpha$-pH curve, i.e., the effect of electrical repulsion is more predominant than that of salt-linkages.

When salt is present in the substrate, however, the maximum in the W-shaped $(A)_F$-pH curve disappeared and the curve had a minimum $(A)_F$ region between pH 5.6 and 8.0 which is parallel to the pH axis (Fig. 3). As described above, salt ions have the effect of reducing the electrostatic interaction between $-NH_3^+$ and $-COO^-$ ions. Therefore, it is very probable that a maximum point which should appear in the $(A)_F$-pH curve, is depressed by salt ions and so the portion corresponding to the $\alpha_L \cdot \alpha_G$-pH curve which

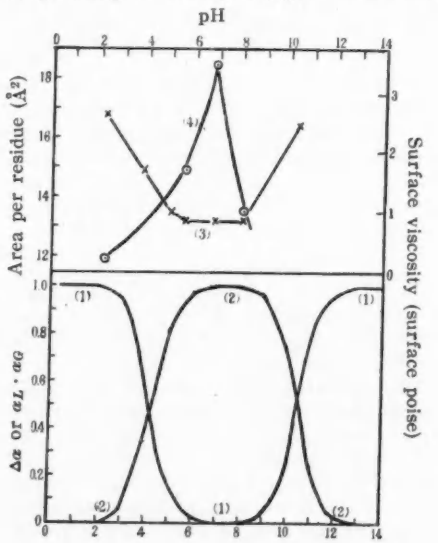

Fig. 9. (1) $\Delta\alpha$-pH, (2) $\alpha_L \alpha_G$-pH, (3) $(A)_F$-pH, (4) $(\eta)_A$-pH curves.

17) J. T. Davies, *Biochim. et Biophys. Acta*, **11**, 165 (1953).
18) M. Joly, "Surface Chemistry" (*Research Supplement*), Butterworth, (1949) p. 157.
19) K. Inokuchi, This Bulletin, **26**, 500 (1953).

represents the term of salt-linkages, disappears. Then as shown in Fig. 3 the $(A)_F$-pH curve has only the portion corresponding to the $\Delta\alpha$-pH curve. Ellis and Pankhurst[20] showed that the $(F)_A$-pH curve obtained with collagen films, showed a maximum at pH 2.2 and sodium chloride in the substrate caused the maximum to be depressed and finally to disappear. The $(\eta)_A$-pH curve has a maximum point at pH 6.8 and corresponds to the $\alpha_L \cdot \alpha_G$-pH curve. This fact also supports the consideration that the surface viscosities depend markedly on the number of inter- or intra- molecular salt likages. The $(A)_F$-pH, $(\eta)_A$-pH, $\Delta\alpha$-pH and $\alpha_L \cdot \alpha_G$-pH curves are shown together in Fig. 9.
These relationships show that the isoelectric point of the copolypeptide lies near pH 6.8.

Summary

By studying the surface pressure-area and surface viscosity-area curves of the copolypeptide of L-lysine, L-phenylalanine and L-glutamic acid over a range of pH values and salt contents in the substrate, the following four distinct results were obtained:

(1) When the concentration of potassium chloride in the substrate was kept constant (0.07 M/litre), the $(A)_F$-pH curve has a minimum area region between pH 5.6 and 8.0 which is parallel to the pH axis and this region corresponds to the isoelectric band of this copolypeptide at this salt concentration. The width of this band was the function of the salt concentration; when the salt content was increased this band became wider.

(2) When the pH's of the substrates was kept constant (pH 2.2), the F-A curves were more expanded at low salt concentrations. This fact could be interpreted by the increment of surface pressure due to the free energy of the electrical double layer which is formed between the ionized groups of the monolayer (NH_3^+ ions) and the counter ions (Cl^- ions). The values of surface potentials calculated from the F-A curves and from Gouy's equation agreed with each other.

(3) The surface viscosities became higher when the salt concentrations in the substrate at constant pH's were decreased and became maximum at its isoelectric point. The surface viscosity depends markedly on the number of inter- or intra-salt-linkages between $-NH_3^+$ and COO^- ions and not on the shape of each polymer molecule.

(4) The $(A)_F$-pH and $(\eta)_A$-pH curves could be interpreted in terms of effective free charges and the number of salt-linkages.

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20) S. C. Ellis and K. G. A. Pankhurst, *Nature*, **163**, 600 (1949); *Trans. Faraday Soc.*, **50**, 82 (1954).

Heats of Combustion and Formation of Some Organosilicon Compounds

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Recently the heats of combustion of organosilicon compounds have been reported by a few investigators[1,2,3,4] using the bomb calorimeter. We measured the heats of combustion of organosilicon compounds in order to derive the bond energies between silicon and other elements. In this paper we shall summerize the conditions of complete burning of organosilicon compounds and the data obtained in our measurements for the heats of combustion of the five following substances; i.e. dimethyl diethoxysilane $(CH_3)_2Si(OC_2H_5)_2$, di-*n*-propyl diethoxysilane $(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$, diethyl silanediol $(C_2H_5)_2Si(OH)_2$, hexamethyl cyclotrisiloxane $[(CH_3)_2SiO]_3$ and hexaphenyl cyclotrisiloxane $[(C_6H_5)_2SiO]_3$.

1) H. Reuther, *Chem. Tech.* (*Berlin*), **2**, 331 (1950).
2) S. Tannenbaum, S. Kaye and G. F. Lewenz, *J. Am. Chem. Soc.*, **75**, 3753 (1953).
3) R. Thompson, *J. Chem. Soc.*, 1953 1908.
4) T. Tanaka, U. Takahashi, R. Ōkawara and T. Watase, *J. Chem. Phys.*, **19**, 1330 (1951); **22**, 957 (1954).

Method and Apparatus

The apparatus was the commercial Berthelot Mahler-type bomb calorimeter, incorporating a 300-ml. stainless-steel-made bomb and a Beckmann thermometer. The calorimeter was set in the thermostat (20±0.2°C), and it was held for an hour in the thermostat before measurement. The temperature rise in the calorimeter was measured through the magnifying-glass attached in front of the thermometer, using a telescope. In order to prevent "sticking" of the mercury of the thermometer, the capillary was continuously kept in a slight vibratory motion[5], that is, the thermometer was ticked by an electromagnetic instrument, placed over the top of it, 150 times per minute, and read with an accuracy of 0.001°C.

Iron wire was employed as the ignition medium, and the value 1490 cal./g. was adopted for the heat of its combustion[6]. For the complete burning of solid organosilicon compounds it was not a desirable method to burn the tablet. The silica produced during the early stage of combustion floated over the surface of the tablet so that there was no access of oxygen beneath it and incompletely burnt residues were left on the base of the crucible. Each solid sample was stuffed into a bag of Ganpi-paper, which was burned with it. The heat of combustion of Ganpi-paper was found to be 3971 cal./g.

After some preliminary work on the method of burning under various pressures, it was successfully found to burn completely under 30 atm. pressure. Before each combustion 1 ml. of water was in the bomb, which was then filled with pure oxygen up to the pressure of 30 atm. at 20°C. In our experiments the air initially present in the bomb was not driven out by filling the bomb with oxygen, bacause of the considerable volatility used for measurements. Accordingly there was always present a small amount of nitrogen within the bomb and the nitric acid produced in the combustion process was titrated with N/14.55-sodium carbonate solution. The magnitude of the thermal correction for this nitric acid, calculated on the basis of an evolution of 14.55 kcal./mole of aqueous nitric acid formed[6], was about 10 calories. The corrected temperature rise was calculated by the method described by Dickinson[7].

To determine the water equivalent of the calorimeter at 20°C, we used the value 6319.0 cal./g.[8] for the heat of combustion of standard benzoic acid (Kahlbaum, *zur Analyse*). Eight calibration experiments of calorimeter were performed with these materials, and its water equivalent value was determined to be 2348 cal./degree (the relative mean deviation ±1.0 cal./degree).

Complete Burning of Liquid Compounds.—Reuther[1] measured the heats of combustion of six organosilicon compounds. However, it is difficult to understand why he did not refer to the technique for the combustion of liquid. For the purpose of complete combustion of polydimethyl siloxane, which could be itself employed as the promoter, Thompson[3] divided the sample into two glass ampoules of nearly the same volume, the more breakable one of which was collapsed at an oxygen pressure of several atm. to produce a pool of liquid in the crucible, and the other stronger ampoule was burnt after firing, owing to the heat produced by the combustion of the liquid pool. But in our experimemt, when the weaker ampoule collapsed, a portion of liquid was scattered, and the liquid attached to the inside surface of the bomb ended in incomplete combustion.

In our experiments the liquid samples were sealed into a thin walled glass ampoule of soft glass. We filled up the ampoule with the liquid so that there might be no air left within it and so that the ampoule might remain filled up at the temperature in the calorimeter. We performed its preliminary ignition by using a cotton string tied to an iron wire, the string being soaked with promoter which was kept in touch with the ampoule. In the combustion measurements of volatile carbon compounds Moore and his coworkers[9] employed specially formed glass capsules, 0.5 to 0.8 ml. in volume and 0.065 to 0.085 g., in empty weight while in our experiments the ampoules were of a single spherical form and the relation of weight to volume was similar to Moore's. The ampoules must be made so as to withstand the oxygen pressure (30 atm.) within the bomb, and also when one weighed more than 0.100 g. it tended to explode on ignition, and then the liquid therein was splashed out of the crucible resulting in incomplete burning. In our combustion measurements about 0.02 g. of liquid paraffin was used as a promoter, and its heat of combustion was found to be 10,868 cal./g. as the average of six measurements. Even under these conditions about half the experiments ended in incomplete combustion, so it was found to be necessary to carry out 10 or more experiments before several consistent values were obtained.

Materials.—Dimethyl diethoxysilane was prepared as follows; the Grignard solution was added drop by drop to diethoxy dichlorosilane diluted with ether for three hours[10,11]. For the preparation of di-*n*-propyl diethoxysilane, the procedure of addition was reversed, that is, diethoxy dichlorosilane dissolved in dry ether was dropped into the Grignard solution for an hour while keeping the reacting mixture below 10°C under cooling and vigorous stirring[10]. Hexamethyl cyclotrisiloxane[12] and hexaphenyl cyclotrisiloxane[13] were prepared by the hydrolysis of dimethyl dichloro-

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11) M. Kumada and T. Tarama, *J. Chem. Soc. Japan, Ind. Sec.*, **54**, 213 (1951), (in Japanese).
12) W. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).
13) C. A. Burkhard, ibid., **67**, 2173 (1945).

silane and diphenyl dichlorosilane, respectively. Another was prepared according to the method of Digiorgio et. al.[14] The physical constants of these samples used for the measurements are shown in Table I.

TABLE I

PHYSICAL CONSTANTS OF THE SAMPLES USED FOR COMBUSTION MEASUREMENTS

Sample	b.p. °C/mm Hg	m.p. °C	d_4^{20}	n_D^{20}	MR_D found	MR_D calcd.
$(CH_3)_2Si(OC_2H_5)_2$	113/760	—	0.8410	1.3815	41.10	41.00
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$[a]	85/20	—	0.8558	1.4100	59.10	59.26
$(C_2H_5)_2Si(OH)_2$[b]	—	96	1.134	—	—	—
$[(CH_3)_2SiO]_3$	134/760	64	—	—	—	—
$[(C_2H_5)_2SiO]_3$[c]	290-300/1	190	—	—	—	—

Anal. a) Si % found 13.5, calcd. 13.7 b) C % found 39.86, calcd. 39.97; H % found 10.12, calcd. 10.07. c) Si % found 14.20, calcd 14.16.

Results and Discussion

By complete burning, gaseous carbon dioxide, liquid water and silicon dioxide evolved as the end products. The completeness of combustion was ascertained by visual inspection of the bomb contents for traces of black or yellow materials[15], and sometimes by chemical analysis. The experimental data for the combustion of dimethyl diethoxysilane are presented in Table II.

TABLE II

THE EXPERIMENTAL DATA FOR DIMETHYL DIETHOXYSILANE AT 20°C

Wt. of sample g.	Total heat evolved cal.	Σ cal.	Σ' cal.	$-\Delta U_B$ cal./g.	Δ cal./g.
0.2530	2177.1	26.5	245.9	7528	− 8
.2650	2406.9	18.0	389.0	7547	+11
.2848	2461.4	20.3	297.7	7526	−10
.2945	2652.2	18.3	412.9	7542	+ 6
.3271	2726.5	19.1	240.3	7542	+ 6
.3316	2904.7	20.6	386.8	7531	− 5
			mean.....7536 (±0.1%)		

The energy evolved per gram at 20°C is represented by $-\Delta U_B$ and the deviations of the individual runs from the mean by Δ. Σ is the sum of the calorific values from nitric acid, iron wire used as the ignition medium, and Joule's energy due to the electric current. Σ' is the sum of the heats of combustion of the promoter and the cotton string. The detailed experimental data for the remaining four samples have been omitted here, involving an overall uncertainty of not more than ±0.1% in relative mean deviation.

Table III contains the summary of the experimental data for the heats of combustion of five substances together with some important thermal data calculated therefrom. The number of satisfied combustion measurements in each case are given in the third column. The values of the bomb process were then recalculated per mole and corrected to the standard constant-volume process where the reactants are at 1 atm. pressure by means of Washburn's equation[16]. The energy evolved in this hypothetical standard process was denoted in Table III by the symbol $-\Delta U_R$. From this quantity the heat evolved in the isobaric process at 1 atm., $-\Delta H_c$, was obtained by the addition of the proper work term. Finally, the heats of formation, $-\Delta H_f°$ (obs.), of these five substances from the standard

TABLE III

HEATS OF COMBUSTION AND DERIVED DATA FOR FIVE COMPOUNDS

Compounds	Mol. wt.	No. of satisfied combustion	$-\Delta U_B$ cal./g.	$-\Delta U_R$ kcal./mol.	$-\Delta H_C$ kcal./mol.	$-\Delta H_f°$ kcal./mol. obs.	calcd. from Pauling's data	calcd. by Gilman and Dunn	calcd. by Thompson
$(CH_3)_2Si(OC_2H_5)_2$	148.25	6	7536	1117	1119	200	180	198.3	214
$(n\text{-}C_3H_7)_2Si(OC_2H_5)_2$	204.35	6	8552	1747	1751	217	205	226.7	233
$(C_2H_5)_2Si(OH)_2$	120.20	3	6495	781	782	212	193	228.2	228
$[(CH_3)_2SiO]_3$	222.38	5	6314	1404	1407	396	357	421.9	463
$[(C_6H_5)_2SiO]_2$	594.78	4	8086	4805	4810	225	151	—	216

14) P. A. Digiorgio, L. H. Sommer and F. C. Whitemore, ibid., 68, 344 (1946).

15) L. H. Long and R. G. W. Norrish, *Proc. Farad. Soc.*, A241, 587 (1949).

16) E. W. Washburn, *Bur. Standards J. Research*, 10, 525 (1933).

elements (gaseous H_2 and O_2, graphitic C, and metallic Si) were calculated from $-\Delta H_c$ by using -68.32[17], -94.05[17] and -208.14[3] kcal./mole for the heats of formation of water, carbon dioxide and amorphous silica, respectively.

Then, we calculated $-\Delta H_f^\circ$ (calcd.) in Table III by using the following data in accordance with the pressumption mentioned below: Data—Heats of atomization of elements; 85.0, 59.1, 51.7, and 124.3 kcal./g.-atom[18] for Si, O, H and C. Bond energies; 87.3, 57.6, 89.3, 58.6, 100 and 110.2 kcal./mole[18] for C-H, Si-C, Si-O, C-C, C=C and O-H, respectively. Resonance energy for benzene nucleus; 39 kcal./mole[18]. The heat of sublimation for hexamethyl-cyclotrisiloxane was found to be 13.2 kcal./mole by Osthoff, et. al.[19] The heats of vaporization for other compounds were presume from Trouton's Rule, and the heats of fusions were assumed to be one-tenth of those of vaporization.

As is shown in Table III the differences between the observed and calculated values of the heats of formation are not small. Uncertainty in the Si-O and Si-C bond energies proposed by Pauling may be the most probable reason for such disagreement.

The values of 52.0 and 59.2 kcal./g.-atom are now generally accepted for the heats of atomization of hydrogen and oxygen, respectively[20]. The corresponding value for carbon is controversial. Direct and various indirect measurements give varying values which fall into three main groups centering around 124,[21] 140[22] and 170[23] kcal./g.-atom. The value of silicon is in even greater doubt. Gilman and Dunn[24] calculated the Si-C and Si-O bond energies using the values 170 and 102 kcal./g.-atom for the heats of atomization of carbon and silicon, respectively, from the heats of formation of carborundum and silica. The resulting values are as follows: Si-C, 75.0; Si-O, 106 kcal./mole. Thompson[3] measured the heats of combustion of some polydimethyl siloxane, and calculated as 64 and 117 kcal./mole for the Si-C and Si-O bond energies from his results. (These values correspond to the following heats of atomization: C, 171.7; Si, 88.04 kcal./g.-atom). They also calculated the heats of formation of dimethyl diethoxysilane etc. These results are shown in Table III and comparatively near to the observed values except those of cyclic compounds.

However, the bond energies obtained by Gilman and Dunn were those derived from the heats of formation of silica and carborundum. It is also very desirable to derive these corresponding bond energies from the organosilicon compounds. The combustion measurements carried out by Thompson[3] contain considerable deviations, so we are not satisfied with bond energies derived from his measurements.

The compounds used here in our measurements, except hexamethyl cyclotrisiloxane, have such a large number of C-C and C-H bond etc. that Si-O and Si-C bond energies calculated from them turn out to be small differences between large quantities, so that they may be unreliable.

Recently we have measured the heats of combustion of some methoxy-polysilane and -polysiloxane, and calculated their heats of formation. The details will soon be published.

Summary

1. A bomb calorimeter has been used for the measurements of the heats of combustion of the following five compounds at 20°C and at constant volume: dimethyl diethoxysilane, di-*n*-propyl diethoxy silane, diethyl silanediol, hexamethyl cyclotrisiloxane and hexaphenyl cyclotrisiloxane.

2. From these experimental results the corresponding heats of combustion and formation at constant pressure have been calculated, and the latter values were compared with the calculated values of the heats of formation derived from the data of the bond energies.

The authors wish to express their sincere thanks to Mr. Kumada, Osaka City University, and Mr. Nozakura, Osaka University, for the preparation of these samples.

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Studies on Molecular Structure by the Measurement of the Dielectric Constants of Gases and Vapors. I. Construction of an Apparatus and the Dipole Moment and the Molecular Structure of 1, 1-Dichloroacetone

By Takehiko CHIBA

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The measurement of dipole moment is one of the most powerful tools for the study of molecular structure. However by the dilute solution method usually employed it is difficult to obtain the true dipole moment of free molecules. The determination of atomic polarization and the measurement of the moment for the substances which are insoluble in nonpolar solvents as well as those which have a moment of small magnitude can only be made by a gas method. In spite of its importance, gas measurements reported so far are very scarce, because a very high precision is required in this method compared with the solution method. The purpose of this research is to study many interesting problems on molecular structure by precise determination of the dielectric constants in the gaseous state.

The present paper deals with the details of the construction of the apparatus and the result of the measurement of the dipole moment of 1,1-dichloroacetone.

I. Apparatus

The measuring apparatus is shown in Fig. 1,

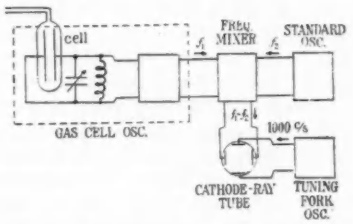


Fig. 1. Block-diagram of the measuring system.

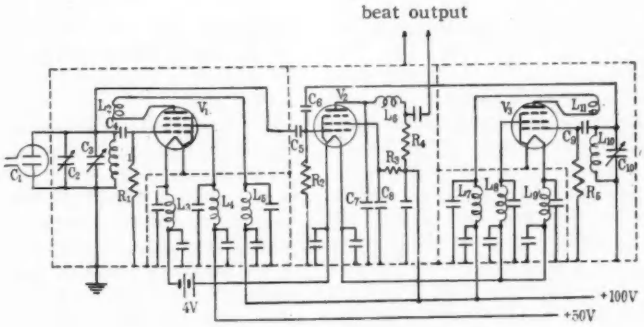


Fig. 2. Oscillators and mixer circuit.

C_1 Gas cell
C_2 Precision condenser
C_3 Variable air condenser (max. capacity, ca. 90$\mu\mu$F)
C_4, C_9 100$\mu\mu$F
C_5, C_8 ~1$\mu\mu$F
C_7 250$\mu\mu$F
C_8 0.01μF
C_{10} Variable air condenser (max. capacity, ca. 860$\mu\mu$F)
All the other capacitors have values of 0.1μF.

R_1, R_5 200kΩ
R_2 1MΩ
R_3 100kΩ
R_4 50kΩ

L_1 41 turns of 0.4mm diameter enamel wire space-wound on 60 mm. diameter "steatite" bobbin.
L_2 10 turns of 0.32 mm. diameter silk-covered wire close-wound on the same bobbin as L_1, with L_2 spaced 7 mm. from L_1.
L_{10} and L_{11} same as L_1 and L_2
L_3, L_9 200μH
L_4, L_5, L_6, L_7, L_8 4mH
V_1, V_2, V_3 1N5-GT

which is similar to that employed by Groves[1]. A beat output from two oscillators, one of which is a standard oscillator and the other one which has a gas cell and a precision condenser in its tank circuit, is fed to one deflection plate of a cathode-ray tube, and 1000-cycle output from a tuning fork oscillator to the other plate to form a Lissajous figure on the screen. The change in the cell capacity by the introduction into the cell of a vapor of a sample is measured by the decrease of the capacity of the precision condenser until the figure takes the original form.

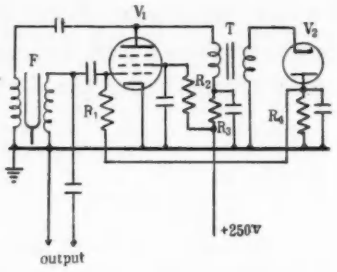
1. Oscillators and Mixer.—The circuit connexion of the oscillators and the mixer is shown in Fig. 2. The gas cell oscillator and the standard one are constructed as similarly as possible, their operating frequency being about one megacycle. The outputs of the two oscillators are fed to the mixer, where a beat frequency is formed.

In the course of the construction of the oscillators, several points are found to be important for maintaining the oscillation frequency in extremely high stability which is necessary for the measurement of a dielectric constant in the gaseous state.

These are as follows: Air condensers exclusively are used for the tank circuit capacity because a mica or titanate condenser gives time drift to the frequency. The tank circuit is designed so as to give the least loss, and, accordingly, both the grid leak and the plate resistance of the vacuum tube circuit are made high (electron coupling circuit is used). The fluctuation of the plate resistance is minimized by not inserting a carbon resistor in the screen grid circuit for potential drop. In order to avoid heat emission from the tube a dry cell tube 1N5-GT is empolyed. The oscillators and the mixer are all battery-operated. They are placed in a wooden box lined with brass plates. The high frequency filters of both high tension and filament supplies for the oscillators are placed in a shielded chassis to avoid inter-oscillator coupling. The earth line is made of a stout brass pipe well soldered to water piping.

The circuit thus constructed proved to be very stable: the drift of the beat frequency was found to be less than one cycle per hour, which corresponds to 2×10^{-4} per cent per hour in the cell capacity change.

The circuit of the tuning fork oscillator is shown in Fig. 3. A slight change in the frequency is noticed by an occasional change



R_1	1MΩ	T	A.F. transformer
R_2	150kΩ	F	Tuning fork
R_3	30kΩ	V_1	6SK7
R_4	500kΩ	V_2	6H6

Capacitors are all 0.01μF.

Fig. 3. Tuning fork oscillator circuit.

in the amplitude of oscillation, a diode amplitude limiter being attached to it.

2. Precision Condenser.—The precision condenser is a micrometer variable condenser[2] shown in Fig. 4. The capacity change

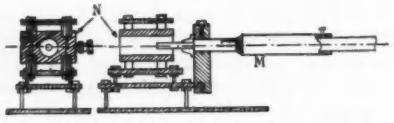


Fig. 4. Precision micrometer condenser.

produced by 1-mm. step of the micrometer condenser is about 0.06μμF, so that a change of capacity can be read to the order of 6×10^{-4}μμF.

3. Gas Cell.—The gas cell is the most important part of the apparatus since the plate surface inevitably comes into contact with various kinds of vapors at high temperatures, and a change in its state affects sensitively the observed value. The cell must be fixed rigidly in order to keep the capacity constant over a long period of time and over a wide range of temperatures. Thus, four kinds of cells shown in Table I are tested. Cell A is that used by Watanabe[3]: the small distance between the plates seems to make serious the capacity instability which occurs in the case of adsorption or condensation of a sample onto the plates. Cell B is constructed with wide gaps but it has mica spacers which were proved to be the cause of an abnormally large increase in the capacity recorded even with far less filling of a sample vapor below its saturation pressure. Cells C and D are constructed so as to eliminate these shortcomings. The

1) L. G. Groves, *J. Chem. Soc.*, 1939, 1144.

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3) I. Watanabe, *Bull. Inst. Phys. Chem. Research (Tokyo)*, 20, 681 (1941).

TABLE I

DATA OF THE GAS CELLS USED

	Plate material	Diam. (mm.)	Length (mm.)	No. of plates	Gaps (mm.)	Spacing insulator	Capacity ($\mu\mu$f)
A	Nickel	45	130	4	approx. 1	Mica	approx. 540
B	Brass (gold plated)	46	130	5	„ 1.5	Mica	„ 450
C	Nickel	35	120	3	„ 1.3	Glass	„ 160
D	Nickel (gold Plated)	46	137	3	„ 1.3	Glass	„ 200

spacing of these cells is as follows. Short nickel wires are silver-soldered at three points, each 120° apart at both ends of each cylinder plate, these three plates are placed in a coaxial position, and glass beads are melted on three nickel wires at each corner (Fig. 5b). The cell is designed to have a capacity of 150 to 200$\mu\mu$F, since, on account of the high stability of the oscillation, it is unnecessary to use a cell of so large a capacity as was previously thought requisite. The middle plate of Cell D is made 2 mm. shorter than the two other plates and the nickel wires are shielded by small guard pieces to reduce stray capacity. Cell D was found to be the most satisfactory.

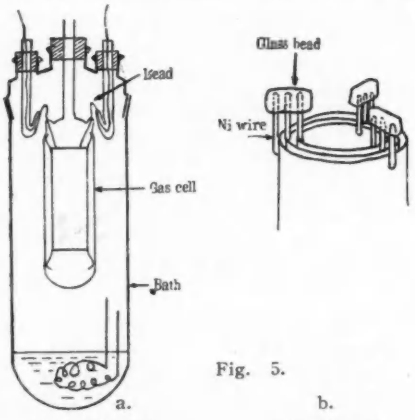


Fig. 5.

a. Gas cell in the vapor bath

b. Spacing of the plates

4. Gas Filling Apparatus and Manometer.—The equipment of gas filling as shown in Fig. 6 is constructed as a modification of Groves' method[1]. A sample in gaseous state is introduced from the cock C_2, while that in a liquid state is first poured into S, cooled from outside, and the whole system is evacuated. Then the cock C_4 is closed and C_5 opened to admit air through the cock C_6 so that the liquid goes up slowly to the capillary U-tube. The path from the cell to the point P is heated with a nichrome wire

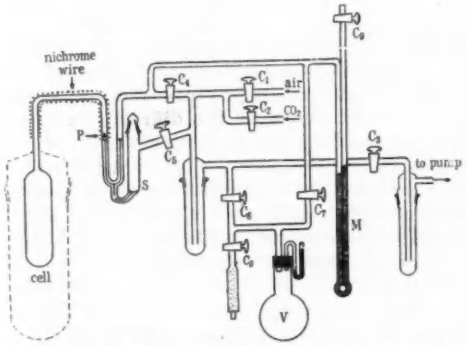


Fig. 6. Apparatus for gas filling and manometer.

to nearly the same temperature as that of the cell. The liquid evaporates at the point P, where a small piece of gold is placed to prevent bumping. Air is admitted from the flow controllable leak-cock C_6 and C_7 so as to keep the liquid in contact with the gold piece, whereby the velocity of the air flow is so adjusted that the liquid meniscus in the manometer side of the U-tube remains at about the middle. Fine pneumatic control is facilitated by connecting cocks, C_6 and C_7, to an air reservoir, V, the pressure in which is kept at about 15 to 30 cmHg. When a desired amount of the vapor is introduced, the two cocks are closed after bringing the liquid menisci of both arms to an equal level; the pressure of the vapor is then directly read by the manometer. The measurement is repeated by evacuating the whole system, condensing the vapor at S, and then carrying out the same operation as stated above. For a sample having a rather high vapor pressure at room temperature, the measurement becomes difficult since it readily condenses on the manometer wall.

5. Vapor Bath.—The cell is maintained at a constant temperature by the use of a vapor bath thermostat (Fig. 5a). Since the lead-wires to the cell are stretched in the vapor of the bath, dew-drops condense on them, followed by a rapid change in stray

capacity disturbing a stationary Lissajous figure at a balancing point. This difficulty is eliminated by covering the lead with glass tubes so that dew does not touch the leads directly (Fig. 5a).

Methanol, benzene, heptane, toluene, xylene, bromobenzene, and decaline are employed for the bath at 65°, 80°, 98°, 111°, 140°, 156° and 192°, respectively.

II. Calibration and Measuring Procedures

1. Calibration of the Micrometer condenser.—It is not necessary to know the absolute capacity of the micrometer condenser accurately, but its linearity must be checked. This is done by observing at each point of the micrometer the difference of the two micrometer readings which occur when the oscillation frequency shifts from a constant frequency to one higher by a given frequency (for instance, 100 cycles). The actual procedure is conveniently carried out by employing two tuning fork oscillators of 1000 and 700 cycles, respectively, and adjusting the beat frequency first to the first overtone of 1000 cycles and then to the second one of 700 cycles. By this procedure it is found that the deviation of capacity from linearity is less than 0.2 percent in the region of 8 to 23 mm. of its readings.

2. Measuring Procedure.—A sample is first introduced to a few mmHg, p_1, by the method described above, and the micrometer reading of the condenser is taken, l_1. The vapor is again filled to the pressure p_2, and the micrometer reading l_2 is taken. The polarization, P, is then given by

$$P=\frac{1}{3}\times\frac{\Delta l}{l_0}\times\frac{RT}{\Delta p}=20790\times\frac{\Delta l}{\Delta p}\times\frac{T}{l_0},$$

where $\Delta l=l_2-l_1$, $\Delta p=p_2-p_1$, T is the absolute temperature of the vapor, and l_0 is the cell constant in the unit of capacity of 1 mm. of the micrometer condenser. l_0 is determined by known substances. Air and carbon dioxide are convenient for this purpose, but these substances have such small polarizations that measurements at several hundred mm. filling have to be carried out. Usually, however, gradual capacity change is observed in such cases, resulting in large fluctuation of l_0 values observed. Therefore mesitylene, on account of its moderate vapor pressure, is used for this purpose and l_0 is measured at three temperatures, 111°, 141°, and 192°. The measured values are constant within experimental errors, l_0 is taken to be their mean value, i. e. 3545 mm. in Cell D.[4] The additional check of the cell constant is made at room temperature using carbon dioxide with a large number of observations of different Δp's. The resultant l_0 is in good accord with the value mentioned above.

The same frequency is used in every measurement, since otherwise a change of the cell constant cannot be avoided if there exists non-negligible inductance between the cell and the other part of the tank circuit.

Samples are filled to about 5 to 15 cmHg. The pressure should not exceed about two-thirds of its saturation pressure, because otherwise abnormally large values are often observed.

In all measurements gas is assumed to be ideal, for the correction of gas imperfection is 0.3 per cent at most and is usually far less than experimental errors. A mean value of $\Delta l/\Delta p$ is used instead of the value extrapolated to zero pressure, since, though it is more rigorous to use the latter, the observed value is always proved to be approximately the same within experimental errors throughout all the values of Δp. In most cases, the error in the observed polarization is 1 to 2 percent in each observation, and the error originates from the pressure readings as well as from the capacity measurement. By several runs of observation, however, it is easy to reduce the error to less than 0.5 per cent.

III. The Dipole Moment and the Molecular Structure of 1.1-Dichloroacetone

1. Experimental and the Result of the Measurement.—1.1-Dichloroacetone was prepared by passing chlorine gas into a mixture of acetone, granulated marble, and water. One volume of the raw product was washed with ten volumes of water to separate monochloroacetone, dried over calcium chloride, and fractionally distilled; b.p. 118–120°C. The main contamination in this product is monochloroacetone, whose absence was confirmed by the observation of the infrared spectrum.

The results of the measurement are given in Table II. The plot of the molecular polarisation, P, against $1/T$ is found to be almost a straight line. If the dipole moment is assumed to be independent of temperature, the inclination of this straight line gives the moment of 1.52 D, and the intercept of this line with the axis of P affords the atomic polarization P_A of 29 cc. It is impossible, however, to allow such a large value to the atomic polarization, since it is well known that in most cases the atomic polarization dose not exceed 10 percent of the electronic polarization, and MR_D of this compound is

4) The polarization of mesitylene is taken to be 41.5 cc.

only 25.8 cc. Thus, by the usual assumption that $P_E+P_A=1.05MR_D=27.1$ cc., it must be concluded that the moment of this molecule increases with the temperature as listed in Table II.

TABLE II

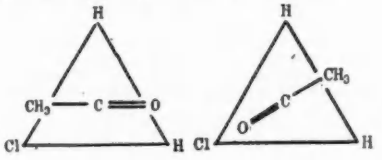
THE OBSERVED POLARIZATION AND DIPOLE MOMENT OF 1, 1-DICHLOROACETONE

$MR_D=25.8$ cc. $P_E+P_A=1.05MR_D$ (assumed)= 27.1 cc.

$T°$	p	n	P	ΔP	μ
K	mmHg		cc.	cc.	D
338.3	65–90	7	92.6	0.5	1.91
371.1	66–117	7	89.0	0.2	1.94
413.3	72–120	7	85.2	0.3	1.99
467.5	85–113	9	81.5	0.4	2.05

p: pressure range of the observations.
n: number of the observations.
ΔP: mean deviation of P.

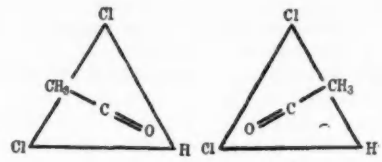
2. Discussion.—It is found that the dipole moment increases with the temperature, which shows clearly that the molecules are distributed over a range of positions with small moment to that with larger moment, and that the former position is more stable than the latter. In the case of monochloroacetone, a small dependence of its moment on temperature was observed by Zahn.[5] The molecular structure of the compounds with a carbonyl group at one end of the axis of internal rotation has been studied extensively through molecular spectra[6] and electron diffraction.[7] According to a spectroscopic study[8] of monochloroacetone, it was concluded, taking Zahn's data into account, that there are two forms of rotational isomers corresponding to the internal rotational angle of 150° and 0°, respectively, taking the *trans*-posistion of the chlorine atom with respect to the methyl group as 0° (Fig. 7a, 7b). It was further



a (more stable) b (less stable)

Fig. 7. Rotational isomers of monochloro acetone.

concluded that in the gaseous state the former is more stable than the latter, the energy difference being estimated as 1 to 2 kcal./mole.[9] The recent molecular spectroscopic study of dichloroacetone[10] revealed that there exist also two rotational isomers in this case. In analogy to the case of monochloroacetone, it may safely be assumed that these isomers take the forms shown in Fig. 2a (the angle θ is taken as 0° at this position) and b ($\theta=120°$). These two forms are considered as well-defined isomers, since they may be separated by a potential barrier of a considerable height due to the steric repulsion between the chlorine atoms and the methyl group.



a (more stable) b (less stable)

Fig. 8. Rotational isomers of 1.1-dichloroacetone.

The dipole moment of this molecule is estimated as follows. The bond moments and the bond angles are taken to be $\mu_{C-Cl}=1.86$ D, $\mu_{C=O}=2.50$ D, $\angle CCCl=\angle ClCCl=$ tetrahedral, and $\angle CCO=123°$. For the correction of the induction effect, the rule suggested by Miyagawa and Morino[11] is used, whereby the amount of induction moment by C=O dipole is taken as being equal to the amount of induction by C-Cl bond dipole multiplied by a factor $\mu_{C=O}/\mu_{C-Cl}=2.50/1.86$. The moments calculated are shown in Table III. As described above, the more stable form

TABLE III

THE CALCULATED MOMENT OF 1, 1-DICHLOROACETONE AT VARIOUS POSITIONS OF INTERNAL ROTATION

θ	0°	30°	60°	90°	120°	150°	180°
μ	1.30	1.53	2.01	2.54	2.96	3.24	3.34

is the one with the smallest moment. Therefore, it should be form (a), corresponding to $\theta=0°$. By assuming the moment of this form to be 1.30 D it is found from the observed temperature dependence of the moment that the difference in energy between the two isomers, ΔE, is about 800 cal./mole., together with the moment of the less stable form of 2.7 D, a value close to the calculated moment for the 120°-form. It should be pointed out that this value of ΔE is smaller than that of mo-

5) C. T. Zahn, *Phys. Rev.*, **33**, 686 (1932).
6) (a) S. Mizushima, et. al., *J. Chem. Phys.*, **20**, 1720 (1952); (b) S. Mizushima, et al., *J. Chem. Phys.*, **21**, 815 (1953).
7) Y. Morino, et al., *J. Chem. Soc. Japan (Pure Chem. Sect.)*, **75**, 647, 721 (1954).
8) Ref. 6(b).
9) T. Miyazawa, private communication.
10) T. Miyazawa, private communication.
11) Y. Morino, I. Miyagawa, and T. Oiwa, *Bochu-Kagaku*, **15**, 181 (1950).

nochloroacetone (1–2 kcal./mole). It may easily be understood from the comparison of Figs. 1 and 2 that the difference in the steric energy between the two forms of dichloroacetone is not so far from that between the corresponding two forms of monochloroacetone. The difference in the dipole interaction energy would also be nearly the same in both cases, if the moment of C-Cl and C=O bonds in the former is equal to those in the latter. Actually, however, the two chlorine atoms in dichloroacetone are attached to the same carbon atom so that the C-Cl bond moments must be reduced considerably by the mutual induction, and consequently the energy difference between the two isomers would also be diminished.

Now the dipole interaction energy in these molecules will be computed in the following way by simple assumptions. The bond dipoles are assumed to converge to dipoles at the contact points of the atomic radii in each bond, their magnitudes being taken to be equal to the corrected bond moments. The assumed dimensions of the molecules are such that $R_{cc}=1.54$ Å, the radius of $-C=0.77$ Å, and of $=C=0.67$ Å, and the bond angles are the same as described above. The calculation shows that the energy difernce of the two isomers is 1.3 kcal./mole in dichloroacetone and 2.2 kcal./mole in monochloroacetone. Because of the approximation of the assumptions used here, it might be too much to expect a quantitative agreement between the calculated and the observed values of ΔE, but it is very interesting to note that the calculated values are parallel to the observed ΔE's. It may, therefore, be concluded from this that the greater part of the energy difference in these molecules is due to the electrostatic energy of dipole interaction, and the lowering of ΔE in dichloroacetone is the result of the reduced moment of the C-Cl bonds by mutual induction. This result is in accord with the conclusion obtained by Mizushima, Morino, and Shimanouchi[13] and that by Miyagawa[14] in the case of haloethanes.

The author expresses his sincere thanks to Professor Y. Morino for his kind guidance in this study and to Dr. I. Miyagawa for his valuable advice.

Summary

An apparatus for the measurement of dielectric constant in the gaseous state is constructed. The electrical circuit is a heterodyne double-beat type, the oscillators with a remarkably high frequency stability are constrcuted. By testing several types of gas cell, it was found that one of them (cell D) can be used satisfactorily for the present purpose. For the gas filling system, a modification of Groves' method is employed. Using this apparatus dielectric constant measurement with an error of less than 0.5 per cent can be obtained.

The dipole moment of 1,1-dichloroacetone was measured in this apparatus. The moment was found to increase with temperature. This increase is attributed to the increase of the more polar isomer (b), which coexists with the form (a). The energy difference of the two isomers was found to be about 800 cal./mole. This value is smaller than that of monochloroacetone, and the lowering of ΔE was considered to be due mainly to the reduced moment of the C-Cl bonds by mutual induction. It was thereby concluded that the energy difference in these molecules is electrostatic in nature rather than steric.

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12) As for the method of determining ΔE from the temperature dependence of the moment, see I. Miyagawa, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, 75, 970 (1954).

13) S. Mizushima, Y. Morino and T. Shimanouchi, *J. Phys. Chem.*, 56, 324 (1952).

14) I. Miyagawa, *J. Chem. Soc. Japan (Pure Chem. Sect.)*, 75, 1169, 1173, 1177 (1954).

Studies on A.C. Polarography. I. Theoretical Treatment

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Introduction

Application of the square wave voltage in the polarographic electrolysis originates from Kemula[1], who employed the rotating switch for the abrupt change of electrode potential. Recently, the polarographic electrolysis, in which the conventional sine wave a.c. voltage is superimposed upon the ordinary d.c. voltage has been elaborated by Breyer and his co-workers[2], and also by Randles[3] and Fournier[4], and their works teem with many interesting findings. Therefore the present authors will discuss this problem mathematically from the general viewpoint.

General Aspects of the Problem

The diffusion processes of the oxidised form (suffix O) and the reduced from (suffix R) are given by Fick's second law of diffusion; i.e.

$$\frac{\partial C_o}{\partial t}=D_o\frac{\partial^2 C_o}{\partial x^2}\ ;\ \frac{\partial C_R}{\partial t}=D_R\frac{\partial^2 C_R}{\partial x^2}. \qquad (1)$$

Here C represents the concentration, D the diffusion coefficient, x the distance from the electrode surface, and t the time. Let ${}^*C_o$ and ${}^*C_R$, respectively, be the uniform initial concentrations of the oxidised and reduced forms, then the initial condition is given by

$$t=0,\ 0\leq x\leq\infty,\ C_o={}^*C_o,\ C_R={}^*C_R. \qquad (2)$$

Upon employing the Laplace-transformation defined by

$$\mathfrak{L}C=p\int_0^\infty e^{-pt}\cdot C(x,t)\cdot dt=u(x,p)$$

we obtain from Eqs. (1) and (2)

$$p(u-{}^*C)=D\cdot\partial^2 u/\partial x^2,$$

which yields the following general integral.

$$u={}^*C+B\cdot\exp\left[-\sqrt{\frac{p}{D}}\,x\right]$$

It follows further that

$$D(\partial u/\partial x)_{x=0}=-\sqrt{pD}\ B.$$

The integral constants B_o and B_R are functions of p, and are determined by the boundary condition. Next, it is quite clear that

$$t>0,\ x=0,\ \phi(t)=\frac{I}{nFq}=D_o\frac{\partial C_o}{\partial x}=-D_R\frac{\partial C_R}{\partial x} \qquad (3)$$

where I, q, F and n represent current intensity, area of the electrode surface, Faraday's constant and the number of electrons associated with the reaction of one molecule of oxidant. Writing

$\mathfrak{L}\phi(t)=\Phi(t)$; $\mathfrak{L}Z_o(t)=B_o(p)$; $\mathfrak{L}Z_R(t)=B_R(p)$,

it is seen that

$$-\sqrt{D_o}B_o=\sqrt{D_R}B_R=\frac{\sqrt{p}\,\Phi(p)}{p},$$

which is inversely transformed into

$$-\sqrt{D_o}Z_o=\sqrt{D_R}Z_R=\int_0^t\frac{\phi(\xi)}{\sqrt{\pi(t-\xi)}}\,d\xi.$$

Thus it follows that the interfacial concentrations of both forms are shown by

$$\left.\begin{aligned}{}^\circ C_o&={}^*C_o-\frac{1}{\sqrt{\pi D_o}}\int_0^t\frac{\phi(\xi)}{\sqrt{t-\xi}}\cdot d\xi\ ;\\ {}^\circ C_R&={}^*C_R+\frac{1}{\sqrt{\pi D_R}}\int_0^t\frac{\phi(\xi)}{\sqrt{t-\xi}}\cdot d\xi.\end{aligned}\right\} \qquad (4)$$

On the other hand, the current intensity is also governed by the rate constants of the electrode processes; thus

$$\phi(t)=\frac{I}{nFq}=\vec{k}f_o{}^\circ C_o-\overleftarrow{k}f_R{}^\circ C_R, \qquad (5)$$

where $\vec{k}$ and $\overleftarrow{k}$ are the rate constants of the cathodic reduction and anodic oxidation, respectively, and f_o and f_R are the respective activity coefficients at the electrode surface.

According to the theory of absolute reaction rate, $\vec{k}$ and $\overleftarrow{k}$ are given by

$$\left.\begin{aligned}\vec{k}&=\vec{k}_s\exp\frac{-\alpha nFV}{RT}\ ;\\ \overleftarrow{k}&=\overleftarrow{k}_s\exp\frac{(1-\alpha)nFV}{RT}.\end{aligned}\right\} \qquad (6)$$

where V denotes the potential of the observation electrode, $\vec{k}_s$ and $\overleftarrow{k}_s$ are the respective rate constants at $V=0$, and other symbols α, R and T are employed in their usual significances. In a.c. polarography, to the dropping mercury electrode is applied the usual constant voltage E and further a sine-

1) W. Kemula, *Collection Czech. Chem. Communs.*, 2, 502 (1930).

2) B. Breyer and F. Gutman, *Discuss. Faraday Soc.*, 1, 19 (1947); B. Breyer, F. Gutman and S. Hacobian, *Austral. J. Sci. Research*, A3, 558, 567 (1950), A4, 595 (1951); B. Breyer and S. Hacobian, ibid., A4, 604, 610 (1951).

3) J. E. B. Randles, *Discuss. Faraday Soc.*, 1, 11 (1947).

4) M. Fournier, *Compt. rend.*, 232, 1673 (1951).

wave a.c. voltage is superimposed thereupon. Thus it is seen that

$$V=E-A\sin\omega t. \tag{7}$$

Namely, both rate constants are also functions of time. The combination of Eqs. (3)... (7) gives the following relationship:

$$\phi(t)=g_1(t)+g_2(t)\int_0^t \frac{\phi(\xi)}{\sqrt{\pi(t-\xi)}}\,d\xi. \tag{8}$$

In this equation the functions $g_1(t)$ and $g_2(t)$ are shown by

$$\left.\begin{aligned} &g_1(t)=k_f{}^*C_O f_1(t)-k_b{}^*C_R f_2(t);\\ &g_2(t)=-\frac{k_f}{\sqrt{D_O}}\cdot f_1(t)-\frac{k_b}{\sqrt{D_R}}f_2(t);\\ &k_f=\vec{k_s}f_O\cdot\exp\frac{-\alpha nFE}{RT};\\ &k_b=\vec{k_s}f_R\cdot\exp\frac{(1-\alpha)nFE}{RT};\\ &f_1(t)=\exp\frac{\alpha nFA\cdot\sin\omega t}{RT};\\ &f_2(t)=\exp\frac{-(1-\alpha)nFA\cdot\sin\omega t}{RT}; \end{aligned}\right\} \tag{9}$$

Thus it is seen that in the case that the electrode potential is a function of time, the resulting diffusion current I is, as shown by Eq. (8), in general demonstrated by Volterra's integral equation of the second kind; this has been already shown in the mathematical treatment of oscillographic polarography of Sevcik-Randles type by Matsuda[5], who has taken the rates of forward and backward reactions into account. The equation of the same form has been discussed also by Delahay[6] dealing with the perfectly irreversible process. Although the solution of Eq. (8) has been mathematically known, the result thereof is too complicated for any practical application.

We will next consider the problem with assumption that both the rate constants $\vec{k_s}$ and $\overleftarrow{k_s}$ are extraordinarily great. Under such a condition, we can legitimately apply the Nernst formula, since the interfacial concentrations of both forms may be then regarded to be always at equilibrium. Therefore we have the following boundary condition.

$t>0,\ x=0,\ K={}^\circ C_R/{}^\circ C_O=({}^*C_R+Z_R)/({}^*C_O-Z_O)$

$$=\exp\frac{-nF(V-E_o)}{RT}$$

$$=\exp\frac{-nF(E-E_o-A\cdot\sin\omega t)}{RT}. \tag{10}$$

In this equation E_o denotes the normal potential of the concerned redox system. Then, upon utilizing the relationship:

$$-\sqrt{D_O}Z_O=\sqrt{D_R}Z_R$$

we can easily obtain the following expression.

$$Z_O=\frac{{}^*C_R-K{}^*C_O}{K+\sqrt{\dfrac{D_O}{D_R}}}=\mathfrak{L}^{-1}B_O(p).$$

Then it is seen that

$$\phi(t)=\mathfrak{L}^{-1}[-\sqrt{pD_O}\cdot B_O(p)]=$$

$$=-\sqrt{D_O}\frac{d}{dt}\int_0^t\frac{Z_O(\xi)}{\sqrt{\pi(t-\xi)}}\cdot d\xi.$$

Namely, we have

$$\left.\begin{aligned} \phi(t)=&-\frac{d}{dt}\int_0^t\sqrt{\frac{D_O}{\pi\xi}}\,X\\ &\times\left\{{}^*C_R-{}^*C_O\beta\exp\frac{nFA\cdot\sin\omega(t-\xi)}{RT}\right\}\times\\ &\times\left\{\sqrt{\frac{D_O}{D_R}}+\beta\exp\frac{nFA\cdot\sin\omega(t-\xi)}{RT}\right\}^{-1}\cdot d\xi;\\ \beta=&\exp\frac{-nF(E-E_o)}{RT}, \end{aligned}\right\} \tag{11}$$

which is the fundamental equation for the instantaneous current intensity due to the a.c. voltage polarization of a reversible electrode.

The above stated theoretical treatment is based on the sound basis, and although the conclusion is mathematically complicated, it may be noteworthy to compare the present theory with the earlier works performed by Randles[3], Breyer with colleagues[2] and others.

Let us at first call to mind the Helmholz theory of electric double layer. For a long time, the electrode surface has been regarded as behaving like an electrostatic condenser. As is well known, the electrolysis with an a.c. voltage is intimately connected with the experimental measurement of the conductivity of electrolytic solution; and in the course of development of the investigations, the terms "polarization resistance" and "polarization capacitance" have been introduced, which indicate the essential rôle of the electrode-solution interface in the electrolysis with a.c. voltage. On the other hand, the electrochemists, who have been studying the "ideal polarized electrode", i.e. the electrode, across the surface of which no charged particle moves, have recently begun to treat the present problem; and especially the works performed by Grahame[7] are decidedly of importance. His opinion may be summarised qualitatively from the a.c. polarographic viewpoint as follows. At a reversible electrode, at which

5) H. Matsuda, Reported at the Discussion Meeting at Nagoya held in November 1952 by the Electrochemical Society of Japan.

6) P. Delahay, *J. Am. Chem. Soc.*, 75, 1190 (1953).

7) D. C. Grahame, *Chem. Revs.*, 41, 441 (1947).

the two rate constants of the electrode processes in forward and reverse directions, i.e. the rate constants of reduction and oxidation, are sufficiently great, by the superposition of an a.c. voltage, the electrode potential is made more negative in a half-period resulting in the predominance of the reduction process of oxidised form at the interface, and thus the reduction product is accumulated considerably at the surface, although some portion of the product may diffuse away. And in the next half-period, the electrode potential becomes so positive that the reductant accumulated at the surface is readily to be oxidised. Hence, corresponding to the periodic change of the electrode potential, the cathodic reduction and anodic oxidation happen alternatively at the electrode surface. Therefore in such a case, a prominant alternating current flows through the surface, so that the electrode surface behaves like a condenser of great capacity. Grahame called such an apparent capacity of electrolytic nature at first "pseudo-capacity"[7] and later introduced a more adequate term "faradayic admittance"[8] in which not only the pseudo-capacity but also the polarization resistance of the electrode surface are taken into consideration.

The above quoted conceptions are to be rationally elucidated by the aid of the integral equation (8) and the Duhamel's integral shown by Eq. (11). Unfortunately these expressions are too complicated to be employed without further modifications; however, the oscillatory character of the electrolytic current is easily to be predicted, since we can legitimately judge that the function $\phi(t)$ may be composed of the periodic functions from the forms of the above equations. This has been really performed in our laboratory by Senda and Tachi[9]; they have transformed the Eq. (8) and (11) into more convenient forms, and thus it is found that the resulting a.c. current is composed of non-alternating d.c. component and a.c. component consisting of many higher harmonic waves.

It must next be mentioned here that Randles' theory[2] concerning such a phenomenon gives a prominent result; i.e. upon assuming the periodic changes of interfacial concentrations, he has derived the equations, by which the rate constant of the electrode reaction can be calculated from the experimental data of a.c. voltage electrolysis. It must however, be pointed out that a weak a.c. voltage of the amplitude of a few millivolts should be employed, owing to the approximate mathematical treatment. Breyer and others[2] have also elaborated the same problem, but is seems that they have not considered the structural change of the diffusion layer with time and regarded the instantaneous current intensity as governed by the value corresponding to the mean diffusion current in the classical polarogram. It may be safe to say that the ordinary polarogram does not show behaviour similar to the characteristic curve of the triode vacuum tube. Nevertheless, their works provide us much experimental information most lavishly and the term "a.c. polarography" has actually originated from them. On the other hand, the articles of Fournier[4] and Kalousek[10] are of special interest, and a more advanced systematic theory for the a.c. polarography will be fully discussed in the succeeding chapter.

Simplified Theory for the A.C. and D.C. Components of Electrolytic Current

(1) **Reversible Electrode.**—The electrode potential in the a.c. polarographic electrolysis is composed of the d.c. voltage E and the sine-wave a.c. voltage $A \sin wt$, as illustrated in Fig. 1(a). Now, let us suppose that the sine-wave a.c. voltage is equivalent to a square-wave voltage, then the electrode potential V shows a change with time as shown in Fig. 1(b); namely,

$$\left.\begin{aligned} E &= \begin{cases} E_1 & \text{for } 0<t<T \\ E_2 & \text{for } T<t<2T \end{cases} ; \\ V(t) &= V(t+2T) ; \\ 2T &= 1/f = 2\pi/\omega . \end{aligned}\right\} \qquad (12)$$

In this case, the suitable amplitude of the hypothetical squarewave voltage may be equal to the effective value of amplitude of the original sinusoidal voltage; i.e.

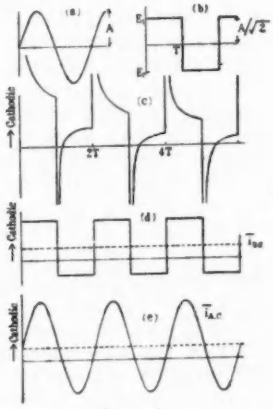

Fig. 1.

8) D. C. Grahame, *J. Electrochem. Soc.*, **99**, 370C (1952).

9) M. Senda and I. Tachi, Reported at the 7th Annual Meeting of the Chemical Society of Japan, held on the 3rd April 1954 in Tokyo.

10) M. Kalousek, *Collection Czech. Chem. Communs.*, **13**, 105 (1948).

$$\frac{1}{2}(E_2-E_1)=\frac{A}{\sqrt{2}} \tag{13}$$

The course of the current-time curve due to the application of a rectangular voltage has been elaborated theoretically by Kambara[11], and an example thereof is given in Fig. 1(c). Further it has been manifested that upon evaluating the respective mean current flowing in each half-period shown by $V=E_1$ and $V=E_2$, we may approximately regard the whole electrolytic current to be the algebraic sum of the constant current $\bar{i}_{D.C.}$, and the square-wave-current $\bar{i}_{A.C.}$, as illustrated in Fig. 1(d); and the current is possessed of the same period $2T$ as the applied square-wave voltage. Let $\bar{i}_1$ be the mean current, that is to be observed when the constant potential E_1 is applied, and let $\bar{i}_2$ be that observed with the constant voltage E_2. Then it can be demonstrated from Kambara's theoretical treatment that

$$\bar{i}_{D.C.}=(\bar{i}_1+\bar{i}_2); \tag{14}$$

$$\bar{i}_{A.C.}=2\left(s\sqrt{f}-\frac{1}{4}\right)(\bar{i}_1-\bar{i}_2)\cdot M(t,\ T) \tag{15}$$

where $S=1.195$ and the meander function $M(t,\ T)$ is defined by

$$M(t,\ T)=\begin{cases}+1 \text{ for } 0<t<T\\ -1 \text{ for } T<t<2T;\end{cases} \tag{16}$$

$$M(t,\ T)=M(t+2T,\ T)$$

Next, we will regard the square wave current, that is shown by Eq. (15) and in Fig. 1(d), as equivalent to a sine-wave alternating current; in order to keep the integrated amount of electricity flowing in each half-period constant, upon employing the familiar factor $\pi/2$, we may be able to describe

$$\bar{i}_{A.C.}=\pi\left(s\sqrt{f}-\frac{1}{4}\right)\cdot(\bar{i}_1-\bar{i}_2)\cdot\sin\omega t. \tag{17}$$

From the above cited somewhat conventional consideration, it may be concluded that when the polarographic electrolysis is carried out under the superposition of sine-wave voltage, the resulting electrolytic current, which is to be represented by a complicated function of time, may be regarded as the sum of two components, i.e. the d.c. component given by Eq. (14) and the a.c. component given by Eq. (17). It follows immediately therefrom that Fournier's polarogram[4] is the register of the d.c. component, and Breyer's current-voltage curve[2] is the recording of the a.c. component. The essential validity of the above conclusion concerning the Fournier's polarogram, has been already reported[11] (see Fig. 2); and further it is expected from the above theory that when we register $\bar{i}_{A.C.}$ against the usual d.c. voltage E, the derivative curve of the reversible polarogram is to be obtained according to Eq. (17), provided that the amplitude of the superimposed a.c. voltage remains constant. This conclusion is quite in harmony with the observations of Breyer's school as well as with the experimental results obtained with the I-F apparatus[12]. It must be, however, pointed out that Breyer and others, although their experimental work is prominent, have shown an irrational consideration in regard to the a.c. component of the irreversible wave; the fast that the irreversible system shows no peak in a.c. polarogram is not due to the less steep inclination at the half-wave point, but it should be essentially ascribed to the irreversible character of the system concerned.

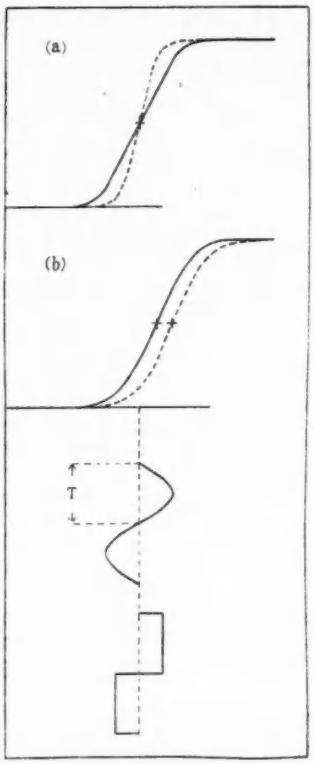

Fig. 2. Fournier's polarogram (a, reversible; b, irreversible).

(2) **Fournier's Polarogram in the Case of Irreversible Wave.**—It has been pointed out that what governs the whole course of polarogram of irreversible redox system is not the interfacial equilibrium concentration of the

11) T. Kambara, This Bulletin, **27**, 527, 529 (1954).
12) M. Ishibashi and T. Fujinaga, This Bulletin, **23**, 261 (1950), **25**, 68, 238 (1952).

depolarizer, but the rate constant at that electrode potential[13]. Now, let us again suppose that the superimposed sine-wave voltage $A \sin wt$ is equivalent to the square-wave voltage of the same frequency, the amplitude of which is shown by $\Delta E = A/\sqrt{2}$ (Fig. 3). Then the rate constant of the cathodic reduction is given by

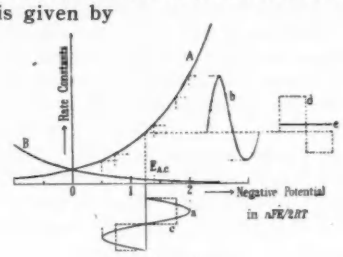

Fig. 3.

$$\vec{k}_{A.C.} = \begin{cases} \vec{k}_E \exp\dfrac{\alpha nF\Delta E}{RT} \\ \quad \text{for } 2nT < t < (2n+1)T\,; \\ \vec{k}_E \exp\dfrac{-\alpha nF\Delta E}{RT} \\ \quad \text{for } (2n+1)T < t < (2n+2)T\,; \end{cases} \tag{18}$$

where n denotes the integer, and $\vec{k}_E$ is shown by

$$\vec{k}_E = \vec{k}_S \exp\frac{-\alpha nFE}{RT} \tag{19}$$

where $\vec{k}_S$ shows the rate constant for $E=0$ [cf. Eq. (6)]. Next writing

$$\Delta\xi = \frac{\alpha nF}{RT} \cdot \Delta E, \tag{20}$$

we can find that

$$\text{Mean value of } \vec{k}_{A.C.} = \vec{k}_E \cdot \frac{1}{2}\left(e^{+\Delta\xi} + e^{-\Delta\xi}\right)$$

$$= \vec{k}_E \cosh\Delta\xi =$$

$$= \vec{k}_S \exp\left\{\frac{-\alpha nF}{RT}\left(E - \frac{RT}{\alpha nF}\ln\cosh\Delta\xi\right)\right\} \tag{21}$$

It has been derived[14] that when a constant potential E is applied to a stationary plane electrode, at which the cathodic reduction proceeds irreversibly, then the resulting rate constant $\vec{k}_E$ determines the instantaneous current intensity i; viz.

$$i = nFq\vec{k}_E^{*}C_O \exp\left(\frac{\vec{k}_E^{2}t}{D_O}\right)\operatorname{erfc}\left(\frac{\vec{k}_E\sqrt{t}}{\sqrt{D_O}}\right) \tag{22}$$

13) H. Eyring, L. Marker and T. C. Kwoh, *J. Phys. Coll. Chem.*, **53**, 1453 (1949); N. Tanaka and R. Tamamushi, This Bulletin, **22**, 187 (1949); R. Tamamushi and N. Tanaka, ibid., 227, **23**, 110 (1950); R. Goto and I. Tachi, *Proc. I. Inter. Polarogr. Congr. in Prague*, Part 1, 69 (1951); N. Tanaka and R. Tamamushi, ibid., 486; M. Kalousek and A. Tockstein, ibid., 563.

14) T. Kambara and I. Tachi, This Bulletin, **25**, 135 (1952).

Further it is known that the polarogram, in which the mean current I is plotted against E, is shown by

$$I = \frac{I_d}{2}\left\{1 + \tanh\frac{-\alpha nF(E-E_{1/2})}{2RT}\right\},$$

which is transformed into

$$E = E_{1/2} + \frac{RT}{\alpha nF}\ln\frac{I_d - I}{I} \tag{23}$$

where I_d denotes, as usual, the mean value of the limiting cathodic diffusion current, and $E_{1/2}$ the half-wave potential of the irreversible wave[13]. It follows from Eq. (21) that the superposition of the a.c. voltage on the constant voltage E is effectively equivalent to the application of the constant voltage $E_{A.C.}$, which is more negative than E as shown in Fig. 3 and is given by

$$E_{A.C.} = E - \frac{RT}{\alpha nF}\ln\cosh\Delta\xi. \tag{24}$$

Therefore, the Fournier's polarogram is the case of irreversible wave is represented by

$$E = E_{1/2} + \frac{RT}{\alpha nF}\ln\cosh\frac{\alpha nF\Delta E}{RT}$$

$$+ \frac{RT}{\alpha nF}\ln\frac{I_d - I}{I}. \tag{25}$$

Namely, by the superposition, the resulting polarogram should be shifted positively (see Fig. 2 and 3); and the half-wave potential of Fournier's polarogram $E_{1/2\text{-Fournier}}$ is more positive than that of the classical polarogram. And the difference between the two half-wave potential is shown by

$$(\Delta E_{1/2})_{A.C.} = E_{1/2\text{-Fournier}} - E_{1/2} =$$

$$\frac{RT}{\alpha nF}\ln\cosh\frac{\alpha nF\Delta E}{RT}. \tag{26}$$

In a case when the amplitude of the superimposed a.c. voltage is of the order of hundred millivolts or more, i.e., $\alpha nF\Delta E/RT \gg 1$, it can be derived approximately that

$$(\Delta E_{1/2})_{A.C.} \simeq \Delta E + \frac{RT}{\alpha nF}\ln\frac{1}{2}. \tag{27}$$

Thus at the room temperature, the shift of half-wave potential is given by

$$(\Delta E_{1/2})_{A.C.} \simeq \Delta E - \frac{0.301}{\alpha n} \times 58\,mV.$$

Hence it is found that there is a linear relationship between the shift of half-wave potential and the amplitude of the superimposed a.c. voltage. On the other hand, for the smaller value of ΔE, it can be readily seen that

$$\ln\cosh\Delta\xi \simeq \ln\left(1 + \frac{1}{2}\Delta\xi^2\right) \simeq \frac{1}{2}\Delta\xi^2;$$

therefore it is found that

$$(\Delta E_{1/2})_{A.C.} \simeq \frac{\alpha nF}{RT} \cdot \Delta E^2.$$

There is no doubt that $(\Delta E_{1/2})_{A.C.}$ becomes zero for $\Delta E=0$, which is a quite rational conclusion. The above developed theoretical consideration has been amply confirmed experimentally and will be reported in our succeeding paper.

Fundamental Theory of A.C. Polarography

It may be concluded from the above stated theory that the essential principle of a.c. polarography is as follows. I.e., when we superimpose an a.c. voltage, the wave form of which may be sinusoidal or rectangular, on the usual polarographic d.c. voltage, then the resulting electrolytic current is an extraordinarily complicated function of time; it is, however, possible to separate the current into the a.c. component and the d.c. component and to observe and record both the components individually. The former is to be called Breyer's polarogram and the latter Fournier's current-voltage curve, and the essential features of Breyer's and Fournier's polarograms are easily comprehensible from the present theory. Thus, from the practical standpoint of polarographic application, the methodology of a.c. polarography is expected to be very important. In the case of the irreversible redox system the a.c. component will show no appreciable peak, which would be advantageous for the elimination of disturbing irreversible waves; and as for the d.c. component, the superposition of the a.c. voltage will surely shift the anodic wave negatively as well as shifting the cathodic one positively, so that at last the separated two waves of the irreversible redox system would unite together, as illustrated in Fig. 4 Although such an example has not yet been reported, it may be safe to say that the superposition of a.c. voltage shows the behaviour of catalyst, since in a half-period it accelerates the cathodic reduction and in another half-period it promotes the anodic oxidation. Next, in the case of the reversible wave, the a.c. component shows a peak, which is to be regarded as the derivative polarogram; and in the case of decreased reversibility, the peak height depends on the degree of reversibility concerned as well as the concentration of the depolarizer; it is well known that the peak height is remarkably dependent of the nature of supporting electrolyte, as reported by Breyer and others.[2] If we record the d.c. component together with the a.c. component and the classical polarogram, then the half-wave potential is to be indicated by the summit potential of the peak and also by the intersection of Fournier's polarogram with the classical one.

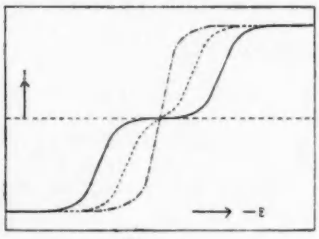

Fig. 4.

So far the a.c. polarography with the a.c. voltage of the constant amplitude has been discussed. It is further possible to make the amplitude vary with time as the d.c. voltage in the ordinary polarography. Then it may be possible with the sine-wave voltage to attain the polarogram of increased sensitivity, which has been shown by I-F apparatus[12] with the aid of rotating switch and current alternator. Further some attractive and characteristic findings obtained with Kalousek's apparatus,[8] which have been cleared up theoretically by Kambara[11], may also be developed by the a.c. polarography, in which the amplitude of a.c. voltage is made to change linearly with time as well as the d.c. voltage.

Addendum[15]

Recently Breyer and Hacobian[16] have published a new theoretical treatment of the present problem, in which the essential role of diffusion in a.c. polarography is legitimately taken into account. The theory deals with the complete reversible electrode reaction. The present authors wish to publish our opinion on the paper later.

Summary

At first the rigorous and orthodox treatment of the polarographic electrolytic current due to the superposition of an alternating voltage upon a constant voltage is shown and the earlier polarographic studies, in which an alternating voltage is employed, are discussed. Next it is shown that in order to treat the a.c. polarography theoretically, we can profitably assume that the superimposed sinusoidal a.c. voltage is equivalent

15) At the request of the editor the present paper was rewritten in a new form. Consequently the new paper by Breyer and Hacobian can be cited here.

16) B. Breyer and S. Hacobian, *Austral. J. Chem.*, 7, 225 (1954).

to the square-wave voltage of the same frequency. In a case when an a.c. voltage, is superimposed upon the usual d.c. voltage, the resulting current becomes a very complicated function of time. It can be shown, however, that the current is the algebraic sum of a.c. component and d.c. component, the latter of which is Fournier's polarogram and the former Breyer's polarogram. Some outstanding characteristics of both components are satisfactorily cleared up, and it demonstrated that in such a manner a rational and systematic explanation of a.c. polarography is given.

The authors wish to express their hearty thanks to Prof. B. Breyer, who has communicated to them the progress of studies carried out in the University of Sydney.

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*Studies on A.C. Polarogroaphy. II. Fundamental Circuit and Some Experimental Results**)

By Mitsugi SENDA, Mitsuko OKUDA and Isamu TACHI

(Received June 12, 1954)

Introduction

A design of a.c. polarographic circuit, where a small alternating potential is superimposed on the usual direct potential applied to the dropping mercury electrode, has been proposed by Breyer and his coworkers[1]. In the circuit designed by them, the a.c. component of the electrolytic current flowing is measured by means of a vacum-tube voltmeter after amplifying the potential drop across a resistor inserted in the electrolytic circuit and the readings of the voltmeter are plotted against the direct potential, giving a.c. polarogram with peak currents at the potentials characteristic to the discharging depolarizers. Recently Ishidate and his coworkers[2] have also showed a new design of a.c. polarograph, in which the amplifier circuit was mainly improved.

In another type of a.c. polarograph, which was first proposed by Kalousek[3], a rectangular alternating potential is superimposed on the usual direct potential with the aid of a rotating switch and the electrolytic current is measured by means of a usual galvanometer by connecting the galvanometer circuit with the switch in a proper way. A similar circuit was also devised by Ishibashi and Fujinaga[4] independently.

In the present paper a design of a.c. polarograph will be given, in which an alternating potential with not only constant but also varying amplitude is superimposed on the direct potential applied to the dropping mercury electrode and the a.c. component of the electrolytic current flowing is recorded against the direct potential automatically on photographic paper. The mean value of the total electrolytic current, which was first observed by Fournier[5] and should be called Fournier's current, is easily obtained by inserting a galvanometer directly in the electrolytic circuit. A brief discussion on the experimental results is also given. All the experiments were carried out at room temperature.

Fundamental Circuit

A schematic diagram of a.c. polarograph designed is shown in Fig. 1. The circuit is composed of three main parts, i.e. an applied voltage source, A, a cell circuit, B, and a device for measuring the resulting current, C. In this figure, A_1B_1 is a potentiometric bridge wound upon an insulating drum, upon which a contact, P_1, slides from B_1 to A_1 with rotation of the drum as in the ordinary polarograph. A_2B_2 is a rheostat and L_1 is a transformer, through which a sinusoidal

* Read at the monthly meeting of the Agric. Chemical Society of Japan held at Kyoto University on 18. July 1953.

1) B. Breyer and F. Gutmann, *Discussion Faraday Soc.* No. 1, 19 (1947). B. Breyer, F. Gutmann and S. Hacobian, *Australian J. Sci. Research* **A3** 558, 567, 595 (1951). B. Breyer and S. Hacobian, Ibid. 604, 610 (1951). We are indebted to Prof. Dr. B. Breyer for sending us reprints of the papers on a.c. polarography.

2) M. Ishidate, T. Isshiki and Y. Masuko, *Japanese Patent*, Application No. 5561/1953.

3) M. Kalousek, *Collection Czech. Chem. Communs.*, **13**, 105 (1948).

4) M. Ishibashi and T. Fujinaga. This Bulletin, **25**, 68, (1952).

5) M. Fournier, *Compt. rend.*, **232**, 1673 (1951).

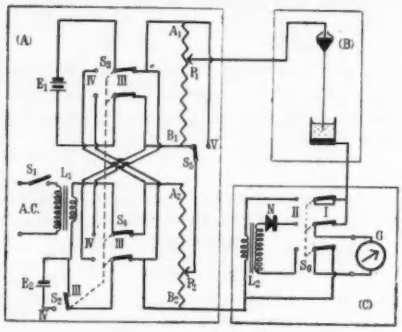

Fig. 1. A.C. Polarographic circuit.

alternating voltage of a definite amplitude is supplied from a 100 v., 60 cycle, A.C. line. Current supplied from a storage battery, E_2, is adjusted so that the direct potential drop across A_1B_1 is equal to the amplitude of the alternating potential drop across it. L_2 is a step-up transformer, N is a crystal rectifier, and G is a moving mirror galvanometer with a conventional shunt. The cell circuit is composed of a dropping mercury electrode inserted into an electrolytic solution and a mercury pool serving as a nonpolarizable reference electrode. Photographic recording of the polarogram is carried out by means of proper mechanical connection between photographic paper and rotation of the drum, as in the Heyrovský-Shikata polarograph.

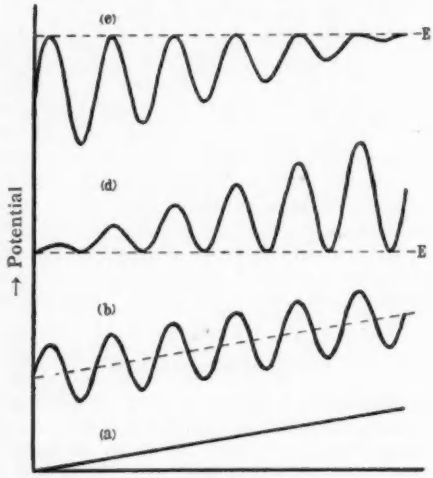

Fig. 2. The change of applied potential with time.
Curve (a): ordinary polarograph.
Curve (b): Fournier's and Breyer's polarograph.
Curve (d): Polarograph with increasing amplitude.
Curve (e): polarograph with decreasing amplitude.
E is the constant applied potential.

The circuit connection illustrated in Fig. 1 represents (a) a circuit operating as an ordinary polarograph. (b) When the switch S_1 is closed, the alternating potential drop of amplitude, ΔV, is produced across the rheostat, i.e.

$$\Delta E = \frac{P_2B_2}{A_2B_2}\Delta V$$

is superimposed upon the d.c. voltage, which, increasing gradually with time or rotation of the potentiometric drum, is applied to the electrolytic cell (Fig. 2-(b)) and the Fournier's polarogram is obtained. Furthermore, (c) connecting the switch S_3 to (II), the Breyer's polarogram, that is a.c. polarogram with constant amplitude, is registered. (d) Connecting the switches S_2, S_3 and S_4 to (IV) and the other switches as in (c), the amplitude of the applied alternating voltage increases gradually with time as is shown in Fig. 2-(d). The constant applied potential, E, is chosen to take the potential value, at which the residual current in ordinary polarogram is obtained, by adjusting the contact of the rheostat. In this case the a.c. component of the electrolytic current has the similar waveform as in the usual polarography[5] and should be called a.c. polarogram with increasing amplitude. (e) Connecting the switch S_5 to (V), the other switches as in (d), and adjusting P_2 so as to produce the applied direct potential at which the limiting current in ordinary polarography is obtained, the amplitude of the applied alternating voltage decreases gradually with time as is shown in Fig. 2-(e) and the a.c. polarogram with decreasing amplitude is obtained[6].

In the latter two cases the so-called base current, i.e. a.c. polarogram of empty solution changes considerably with the amplitude of the applied alternating potential but this change of the base current is easily compensated by connecting P_2 and B_2 to the galvanometer circuit by a resistor of large value, because the base current changes linearly with the amplitude, if the differential capacity of electrical double layer at the mercury-solution interface remains almost constant in the potential range, over which the polarograms are taken. All of the polarograms shown in Fig. 4 were taken using this method. Near the electrocapillary maximum potential, however, this condition is not

6) I. Tachi and T. Kambara, This Bulletin, 28, 25 (1955).

fulfilled (Fig. 4-(b) and (d)) and a current eliminator of differential type[7] will be necessary for getting well-defined waves. Polarograms recorded by the present circuit are shown in Fig. 3 and Fig. 4. The sudden change of current intensity in the polarograms (e) and (f) in Fig. 4 (marked by arrows) is due to the sudden decrease of drop time, which occurs at a certain potential governed by the amplitude of the applied alternating potential[8]. In such a case artificial control of drop time is needed.

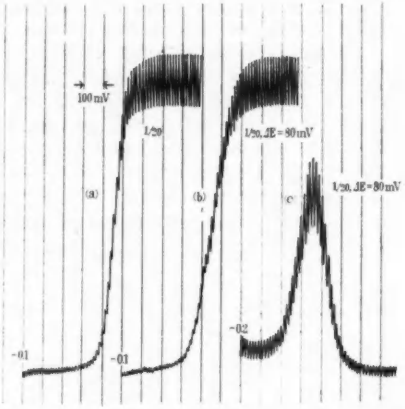

Fig. 3. Ordinary and a.c. polarograms of 10^{-3} M Tl^{+} ion in 0.1 N. KCl solution.
Curve (a): ordinary polarogram.
Curve (b): Fournier's polarogram.
Curve (c): Breyer's polarogram.

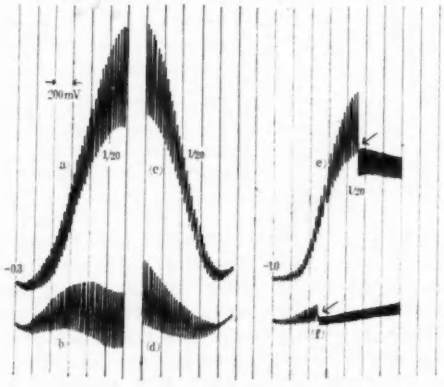

Fig. 4. A.C. Polarogram with varing amplitude.
Curve (a): 1.2×10^{-3} M Tl^{+} ion in 0.1 N KCl soln., with increasing amplitude.
Curve (b): base current of 0.1 N KCl soln., with increasing amplitude.
Curve (c): 1.2×10^{-3} M Tl^{+} ion in 0.1 N KCl soln., with decreasing amplitude.
Curve (d): base current of 0.1 N KCl soln., with decreasing amplitude.
Curve (e): 10^{-3} M Zn^{++} ion in N KCl soln., with increasing amplitude.
Curve (f): base current of N KCl soln., with increasing amplitude.

Effect of Circuit Characteristics on A.C. Polarogram

Because a.c. polarography is a sort of potential-conditioned electrolysis, the total impedance of the electrolytic circuit must be kept as small as possible, so that it is negligible compared with the equivalent impedance of the observed electrode interface. Though the latter is a function of the direct potential, the amplitude of alternating potential, concentration of depolarizer discharging and other factors concerning the electrode reaction, it is usually far less than it is in ordinary polarography. Accordingly this condition must be carefully fulfilled. In the present experiment the total impedance of the electrolytic circuit except the cell circuit was kept at about 500 ohms, which is not small enough when we carry out the experimental study of a.c. polarography, e.g. in a wide range of concentration of depolarizer. In a.c. polarography the resistance of the electrolytic solution can not be neglected, when the electrode impedance is vanishingly small, e.g. the concentration of depolarizer is high. Fig. 5 shows the effect of concentration of supporting electrolyte on the magnitude of a.c. polarographic current. This effect of supporting electrolyte might be partially due to the change of reversibility of electrode

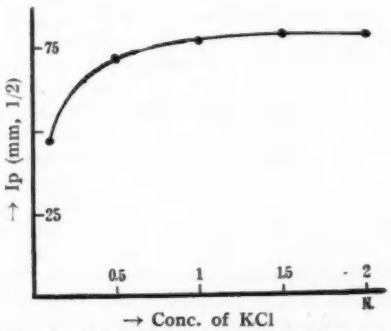

Fig. 5. Effect of concentration of supporting electrolyte on the peak height of a.c. polarographic current of 10^{-3} M Cd^{++} ion in KCl solution.

7) G. Semerano and L. Riccoboni, *Gazz. chim. ital.*, 72, 297 (1942).

8) I. Tachi and M. Okuda, This Bulletin, 27, 310 (1954).

reaction (see below) but, in a large part, due to the resistance of electrolytic solution.

The relation between galvanometer deflection and alternating current flowing across the primary coil of the transformer L_2, is shown in Fig. 6. When the alternating

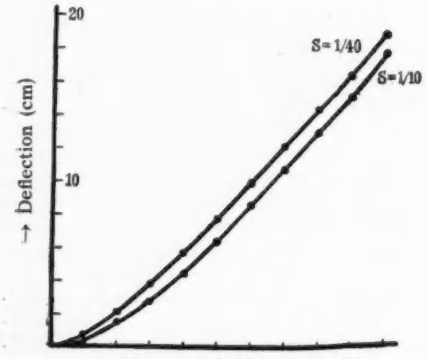

Fig. 6. Characteristics of alternating current detector.

current flowing is negligibly small, the crystal rectifier loses its function. A high gain electronic amplifier is now being constructed in this laboratory.

Effect of Reversibility of Electrode Reaction

In a.c. polarography the reversibility of electrode reaction plays a far more important rôle than it does in the ordinary polarography. Detailed experimental study on the a.c. polarographic behaviour of sufficiently reversible electrode reaction will be reported in the succeeding paper of this series. In the present paper preliminary experimental study on the effect of reversibility will be given.

When the electrode reaction is irreversible, the half-wave potential of Fournier's polarogram is shifted to more positive potential with increasing amplitude of the applied alternating potential. According to the theory developed in the previous paper[8], the difference $(\Delta E_{1/2})_{A.C.}$ of half-wave potentials between ordinary polarogram and Fournier's is given by the equation

$$(\Delta E_{1/2})_{A.C.} = \frac{RT}{\alpha nF} \ln \cosh \frac{\alpha nF}{RT} \Delta E$$

where ΔE is the amplitude of the alternating potential, n the number of electrons required for reduction of one molecule of depolarizer, α the transfer coefficient of reduction process at the electrode and F, R and T are Faraday constant, gas constant and absolute temperature, respectively. When ΔE is larger than a hundred millivolts, $(\Delta E_{1/2})_{A.C.} - \Delta E$ curve becomes a straight line and the tangent of the straight line must be unity. Moreover α could be calculated from the ordinate of the intersection of the straight line and $(\Delta E_{1/2})_{A.C.}$-axis. Experimental results with nickel ion in 0.1 N KCl solution, which is known to be reduced irreversibly at the dropping mercury electrode[9], are given in Fig. 7, where ΔE is plotted in effective value.

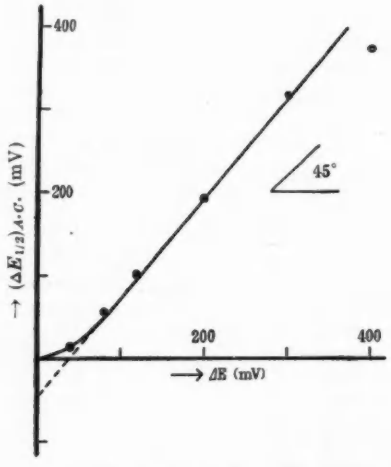

Fig. 7. Shift of the half-wave potential of Fournier's polarogarm with the amplitude of applied alternating potential.

By the graphical extrapolation of the experimental curve, the transfer coefficient was determined to be about 0.3. However, the slope of the experimental curve is slightly steeper than the slope of the theoretical one. This might be attributed to the assumption that the sinusoidal wave was supposed to be equivalent to the square wave.

Randles[10] and others[11,12] have shown that when the amplitude of the applied alternating potential is sufficiently small i.e.

$$\Delta E \frac{\alpha nF}{RT} \ll 1,$$

the electrode interface at equilibrium potential is at the stationary state electrically equivalent to the circuit shown in Fig. 8, where

9) J. Heyrovský, *Discussion Faraday Soc.* No. 1, 121 (1947).
10) J.E.B. Randles, ibid., No. 1, 11 (1947).
11) H. Ershler, ibid., No. 1, 269 (1947).
12) H. Gerischer, *Z. physik. Chem.*, **198**, 286 (1951).

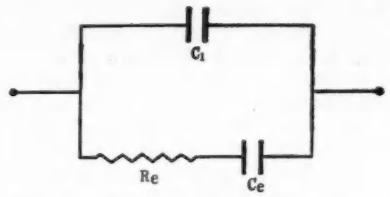

Fig. 8. Equivalent circuit of electrode surface at equilibrium potential at the stationary state.

C_l is the differential capacity of the electrical double layer and C_e and R_e are the capacity and resistance equivalent to the electrode reaction and given by

$$1/\omega C_e = \frac{RT}{n^2F^2} \cdot \frac{1}{qC} \cdot \sqrt{\frac{2}{\omega D}}$$

and

$$R_e = \frac{RT}{n^2F^2} \cdot \frac{1}{qC} \cdot \left(\sqrt{\frac{2}{\omega D}} + \frac{1}{k}\right)$$

respectively, where D is the diffusion coefficient of oxidized and reduced forms, assumed to have the same diffusion coefficient, ω is angular velocity of the alternating potential, k the rate constant of electrode reaction at the equilibrium potential, q surface area of electrode and C is concentration of the depolarizer. From this theory, it is easily recognised that the current intensity of the a.c. component is closely related to the reversibility of electrode reaction. Recently Grahame[13] has developed a more comprehensive theory of a.c. electrolysis and, assuming Ilkovič equation for the diffusion process of depolarizer, he showed that the current intensity at peak potential decreases with decreasing value of k. Fig. 9 shows the Breyer's polarogram and ordinary polarogram of Cd^{++} ion and Z_n^{++} ion in 0.1 N KCl solution; it is known that the reversibility of the former is higher than the latter. In Table I relative values of peak heights of a.c. polarograms of Zn^{++} ions in various supporting electrolytes are given. The experimental results confirm the above theoretical conclusion. Ni^{++} ion in 0.1 N KCl solution shows no appreciable a.c. polarographic wave, which corresponds to its characteristic behaviour in Fournier's polarogram.

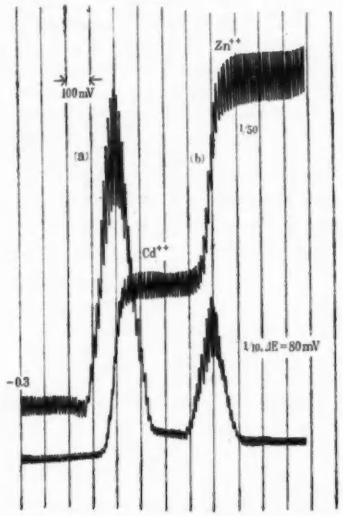

Fig. 9. Breyer's polarogram (Curve-(a)) and ordinary polarogram (curve-(b)) of 10^{-3} M $Cd(SO_4)+10^{-3}$ M $Zn(NO_3)_2$ in 0.2 N KCl solution.

TABLE I

CHANGE OF PEAK HEIGHT OF 10^{-3} M Z^{++} ION WITH THE REVERSIBILITY OF ELECTRODE REACTION

Supporting electrolyte (1 N.)	KNO_3	KCl	KBr	KI
k*) (cm/sec)	3.5×10^{-3}	4×10^{-3}	8×10^{-3}	7×10^{-3}
peak height (%)	71	100	201	570

*) B.E. Conway: Electrochemical data, Elsevier Pub. Co. (1952); see also reference (14).

Applications of A.C. Polarography

The high utility of a.c. polarography in analytical applications has been discussed by Breyer and his coworkers[1], i.e. (a) there is no need to remove dissolved oxygen from the electrolytic solution, (b) small amounts of less noble ions can be determined in the presence of a large excess of noble ions, (c) reduction potentials only 40 mV apart are separable using small alternating voltage, (d) the a.c. polarographic current is greater than the ordinary polarographic current, and the limit of sensitivity is at about 10^{-5} N.

The considerable effect of reversibility of electrode reaction on a.c. polarography leads to another interesting applicability of a.c. polarography as is shown in the following model experiment. In Fig. 10, a-I and II are

13) D. C. Grahame, *J. Electrochem. Soc.*, **99**, 370c. (1952).

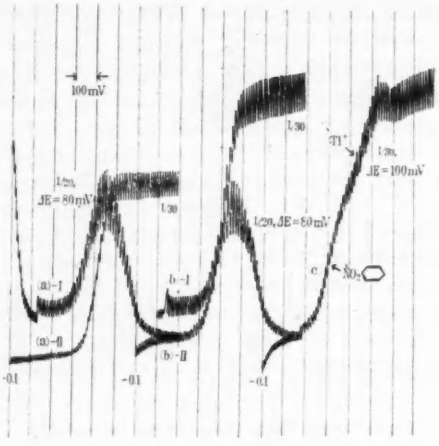

Fig. 10.

Curve (a)-I: Breyer's polarogram of 10^{-3} M $TlNO_3$ in 0.5 N KCl soln. pH=6.

Curve (a)-II: ordinary polarogram of the same solution as (a)-I.

Curve (b)-I: Breyer's polarogram of 10^{-3} M $TlNO_3$+nitrobenzen in 0.5 N KCl soln. pH=6.

Curve (b)-II: ordinary polarogram of the same solution as (b)-I.

Curve (c): Fournier's polarogram of the same solution as (b)-I.

a.c. polarogram and ordinary polarogram of Tl^+ ion, respectively, and b-I and II are the same polarograms, after addition of certain amounts of nitrobenzen to the same solution as (a). Curve (c) is Fournier's polarogram of the same solution as (b). Because the reversibility of electrode reaction of Tl^+ ion is sufficiently high but that of nitrobenzene is considerably low, the magnitude of a.c. polarographic current of the latter is negligible compared with that of the former. Also, because of the positive shift of Fournier's polarogram of nitrobenzene, the completely overlapped wave in b-II has a tendency to separate into two waves in (c). The above experimental results predicate that, when two depolarizers have half-wave potentials lying very close together, or lying even at the same potential, the separate determination is possible, if the degree of reversibility of them is considerably different. Using a.c. polarography for analytical purpose, the effect of the ionic species of supporting electrolytes on the reversibility must be also taken into account. The effect of change of reversibility caused by a minor contamination of surface active substances, which might come into electrolytic solution during sampling, could be avoided by addition of certain amounts of gelatine to the electrolytic solution. Reversibility of electrode reaction, though it decreases by the addition of gelatine, stays almost constant after the concentration of gelatine added attains to a certain range[14]. More detailed experimental as well as theoretical studies on a.c. polarography are now in progress in our laboratory.

Summary

Fundamental circuit for a.c. polarography, in which a.c. polarogram with varying as well as constant amplitude is automatically registered, was shown. And the close relation between reversibility of electrode reaction and a.c. polarographic behaviour of depolarizers was experimentally verified and another applicability of this method was pointed out.

The authors are indebted to Yanagimoto Co. Ltd. for the support of this investigation.

Department of Agricultural Chemistry, Faculty of Agriculture, Kyoto University, Kyoto

14) J. E. B. Randles and K. W. Somerton, *Trans. Faraday* Soc., **48**, 951 (1952).

*Studies on A. C. Polarography. III. Reversible Wave**)

By Mitsuko OKUDA and Isamu TACHI

(Received June 12, 1954)

Introduction

In Part I[1] and II[2] of this study the theoretical treatment of the Alternating Current-Polarography (a. c. polarography) was reported, and in Part III[3] the fundamental circuits together with the results of several basic experiments were communicated. In this article, the experiments concerning the d. c. and a. c. components of electrolytic current due to the reversible electrode reaction observed with the a. c. polarographic equipment, in which a sinusoidal alternating voltage of a constant amplitude is superimposed on the constant d. c. voltage used in the ordinary polarography, will be given and compared with the theoretical conclusion.

As is well known, the mean current $\bar{i}$, which is observed in the ordinary polarography using a dropping mercury electrode, is a function of the electrode potential V, and is given by

$$\bar{i}=\frac{\bar{i}_d}{2}\left\{1+\tanh\frac{nF(E_{1/2}-V)}{2RT}\right\}, \qquad (1)$$

where $\bar{i}_d$ is the mean limiting diffusion current, n the number of electrons associated with the electrolytic reduction, $E_{1/2}$ the half-wave potential, and the other symbols have their usual significances. According to the theoretical treatment given in Part II of this study, in the case that the electrode reaction proceeds reversibly, the mean value, $\bar{i}_F$, of the d. c. component of the a. c. polarographic electrolytic current, i. e. Fournier's polarogram, is shown by

$$\bar{i}_F=\frac{1}{2}(\bar{i}_1+\bar{i}_2), \qquad (2)$$

whereas the mean value of the amplitude of a. c. component, i. e. Breyer's polarogram, is given by

$$\bar{i}_{A.C.}=K(\bar{i}_1-\bar{i}_2). \qquad (3)$$

Let E be the constant d. c. voltage applied to the dropping mercury electrode, and ΔE the amplitude of the superimposed a. c. voltage, then $\bar{i}_1$ and $\bar{i}_2$, respectively, are given by

$$\left.\begin{aligned}\bar{i}_1&=(\bar{i})_{V=(E-\Delta E)};\\ \bar{i}_2&=(\bar{i})_{V=(E+\Delta E)}.\end{aligned}\right\} \qquad (4)$$

K in Eq. (3) is given by $(s\sqrt{f}-1/4)$, in which f is the frequency of the a. c. voltage, and $S=1.192$ is a constant. Because we use a. c. voltage of 60 c/s, K is nearly equal to 9.04. The above theoretical treatment has been based on the assumption that the superimposed sinusoidal alternating voltage is equivalent to the square wave voltage of a suitable amplitude; we employ here the a. c. voltage of sinusoidal wave form. Thus, in the present experiment, the effective value of the superimposed a. c. voltage is regarded to be equivalent to the amplitude of the square wave voltage, and the results are discussed. As the depolarising cation, thallous ion in 0.1 N KCl solution is chiefly employed, since it is well known that the ion shows nearly a perfect reversible behaviour[4,5]; and further cadmium ion is often, according to the necessity, employed, which also shows a high degree of reversibility[4]. Circuit for a. c. polarography, as already reported in Part III of this study, is used. The superimposed a. c. voltage is obtained by lowering the 100 v., 60 cycle a. c. line by means of a transformer and a suitable rheostat divider; the electrolysis is carried out in room temperature at 25°C and the bottom mercury layer was used as the anode, against which the cathode potential is measured. The sensitivity of galvanometer used is 4×10^{-9} Amp./mm./m.

Experimental Results and the Theoretical Consideration

(1) Wave Form of the A. C. Polarogram.—Fig. 1 shows the theoretical a. c. polarograms together with the ordinary polaro-

*) Read at the monthly meeting of the Agric. Chemical Society of Japan held in Kyoto University on the 18th July 1953.

1) I. Tachi and T. Kambara, This Bulletin, 28, 25 (1955).

2) T. Kambara and I. Tachi, ibid., 28 25 (1955).

3) M. Senda, M. Okuda and I. Tachi, ibid., 28 31 (1955)

4) J. Heyrovský, *Discus. Farad. Society*, No. 1, 121 (1947).

5) J. E. Randless, ibid., 11.

gram; and in Fig. 2 and 3 are illustrated the a. c. polarograms observed experimentally. In Fig. 1 curves d and e represent the

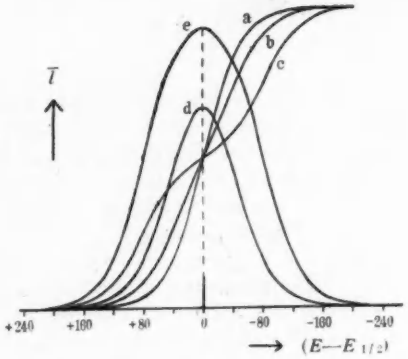

Fig. 1. Theoretical polarograms.
($n=1$, $t=25°C$)
a: ordinary polarogram, $\Delta E=0$mV
b: Fournier's polarogram, $\Delta E=40$mV
c: Fournier's polarogram, $\Delta E=80$mV
d: Breyer's polarogram, $\Delta E=40$mV
e: Breyer's polarogram, $\Delta E=80$mV

a. c. components, where the currents are plotted in $1/K$ unit of the calculated values. As required by the theoretical conclusion shown by the Eqs. (1) and (2), the d. c. component of a. c. polarogram (namely, the Fournier's polarogram) shows the less steep slope than the classical polarogram with the increasing amplitude of the superimposed a. c. voltage, until it begins to split into two steps; and the classical and Fournier's polarograms intersect with each other always at the half-wave point. The experimental results shown in Fig. 2 are in good harmony

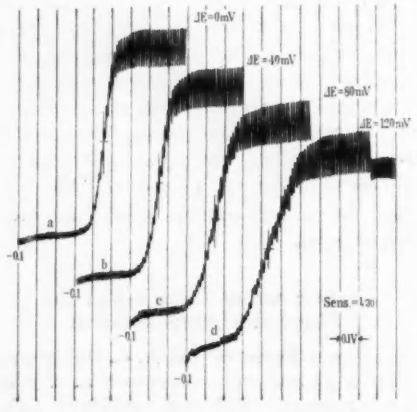

Fig. 2. Observed Fournier's polarogram due to the depolarization of Tl^+. Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCl

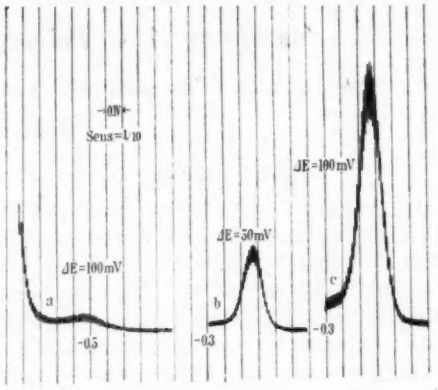

Fig. 3. Observed Breyer's polarogram due to the depolarization of Tl^+.
a: 0.1 N KCl solution
b and c: 2×10^{-3} M $TlNO_3$ in 0.1 N KCl solution

with the theoretical prediction. On the other hand, the a. c. component of the a. c. polarogram (namely, the Breyer's polarogram) is found to show a peak at the half-wave potential, as shown obviously by Eq. (3) and also in Fig. 3. In the case of the Breyer's polarogram, owing to the differential capacity[6] of the electric double layer at the electrode-solution interface, an alternating current governed by the product of the differential capacity and surface area flows, even when there is no depolarizer in the solution (Fig. 3 (a)); thus the recorded alternating current is the vector sum of the alternating current, $\bar{i}_B$, due to the differential capacity, which is to flow in the empty solution, and the electrolytic alternating current, $\bar{i}_{A.C.}$. It is clear that when we observe the Fournier's polarogram, the current due to the differential capacity is not observable by the galvanometer, since the mean value thereof is obviously zero.

It must be mentioned here that the anodic dissolution of mercury affects the a. c. polarogram considerably. Namely, in Fig. 2 (d) the Fournier's polarogram due to the anodic reaction of mercury is observable in the more negative potential than in the case of classical polarogram. Also in Fig. 3 (a) the Breyer's polarogram increases suddenly at the positive potential, where the oscillatory current due to the reversible deposition and dissolution of mercury is of special importance.

It is seen further that the drop time often becomes abruptly short resulting in the sud-

6) D.C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

den decrease in the current intensity; this is found in the ascending parts of the waves shown in Fig. 2 (c) and (d) and in the final part of the wave shown in Fig. 2 (d). This finding seems to be due to the effective decrease in the interfacial tension caused by the superposition of a. c. voltage. The critical potentials, at which such a sudden decrease occurs, lie in both sides of the potential corresponding to the electrocapillary maximum, and furthermore the two critical potentials shift nearly symmetrically with the varying amplitude of the superimposed a. c. voltage, as has been already reported by us[7].

According to the above cited theoretical equation, the half-wave potential of the Fournier's polarogram, denoted by E_F, and the peak potential of the Breyer's polarogram, denoted by Ep, are expected to be identical with the half-wave potential of the ordinary polarogram, independently of the concentration of depolarizer and the amplitude of the superimposed a. c. voltage. Table I gives the experimental results obtained with thallous ion. We can find a fairly good accordance thereof. However, it is found experimentally, that Ep is by ca. 20mV more negative than $E_{1/2}$ and E_F is shifted positively with the increasing amplitude. The reason of such phenomena will be perfectly clarified, when a more exact theoretical treatment, in which the velocity constants of the electrode processes and the transfer coefficient, usually denoted by α, are taken into consideration.

Also the limiting current in the Fournier's polarogram coincides with that of the classical polarogram at a *sufficiently* negative potential. The experimental results shown in Fig. 2 are in harmony with the theoretical prediction. On the other hand the observed peak height in Breyer's polarogram is far less than the theoretical value. This will be discussed in the succeeding section of this report.

TABLE I

COMPARISON OF THE HALF-WAVE POTENTIAL OF FOURNIER'S POLAROGRAM AND THE PEAK POTENTIAL OF BREYER'S POLAROGRAM

Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCl

ΔE (mV.)	$E_{F(V.)}$	$E_{p(V.)}$
0	-0.55_0	
40	-0.54_8	-0.57_0
80	-0.54_5	-0.57_0
120	-0.54_0	-0.57_0

(2) Effects due to the Amplitude of the Superimposed A. C. Voltage.—Fournier has verified experimentally the influence of the frequency of the superimposed a. c. voltage on the d. c. component of the polarographic current, and found that in the case of the reversible electrode reaction the wave form remains nearly unchanged independently of the frequency, provided that the amplitude thereof is kept constant[8]. This is theoretically predicted by Eq. (2). Thus we have investigated the behaviour of d. c. component in the case that the amplitude is varied, while the frequency of 60 c/s is unchanged. As stated above, the d. c. component is at last splitted into two waves with the increasing amplitude employed, while the half-wave point lies unchanged at the original half-wave potential. This can be far more distinctly observed when the wave analysis is carried out concerning the Fournier's polarogram. Fig. 4 gives an example of thallous

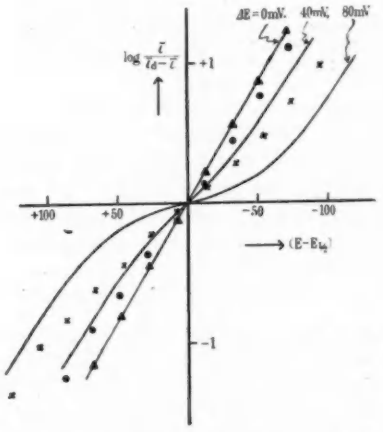

Fig. 4. Wave analysis of the Fournier's polarograms of Tl^+ (for a, b and c in Fig. 1 and 2) by means of the logarithmic plott.

——: theoretical curves

▲ (ΔE=0mV)
● (ΔE=40mV) : experimental values
× (ΔE=80mV)

ion. A small deviation of the experimental observation from the theoretical equation is found, which may be due to the simplified supposition that the applied sinusoidal alternating potential is equivalent to a square wave voltage. The course of the observed current-potential curve, however, runs quite in the same manner to the theoretical curve, indicating the essential legitimacy of the theory.

7) I. Tachi and M. Okuda, This Bulletin, **27**, 310 (1954).

8) M. Fournier, *Comp. rend.*, **237**, 1673 (1951).

In Fig. 5 is given the dependency of the

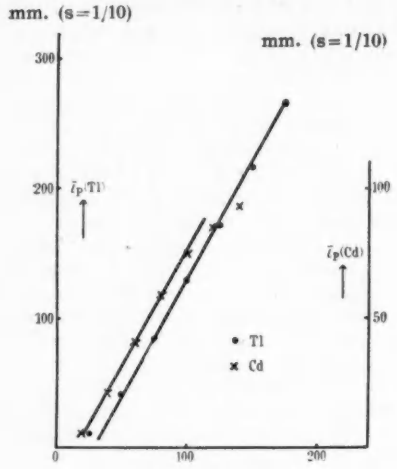

Fig. 5. Peak current vs. ΔE curve.
●: 2×10^{-3} M $TlNO_3$ in 0.1 N KCl
×: 5×10^{-4} M $Cd(SO_4)$ in 0.1 N KCl

peak current intensity of the Breyer's polarogram on the amplitude of the employed a. c. voltage. Ih this diagram each current intensity has been calibrated for the capacity current, which is also observable with the blank solution. From Eq. (3), it follows that

$$\bar{i}_p=[\bar{i}_{A.C.}]_{V=E_p}=A\cdot K\cdot \bar{i}_d\cdot \tanh\frac{nF}{2RT}\cdot \Delta E \quad (5)$$

where A is a constant given experimentally and depends on some characteristic constants of circuit and equipment employed. In the present experiment this constant is about 1/40. This exhibits the relationship between the peak current and amplitude. It is expected therefrom that the slope of $\bar{i}_p$ vs. ΔE curve becomes gradually less steep with the increasing value of ΔE, until $\bar{i}_p$ approaches to a constant value given by $A\cdot K\cdot \bar{i}_d$. The experimentally obtained value with cadmium ion, shows such a tendency, however, not in such a remarkable manner as expected from Eq. (5), and a linear relationship between $\bar{i}_p$ and ΔE is observable in an appreciably wide range. In the case of thallous ion, such a linearity persists even with the amplitude greater than 170 mV. Such a difference between Cd^{++} and Tl^{+} seems to be ascribed to the difference of the reversibility as well as to the difference of number of electrons of the two redox-systems.

(3) Effect due to the Height of Mercury Reservoir.—Variations of the d. c. and a. c. component due to the change of the height of mercury reservoir are illustrated in Fig. 6.

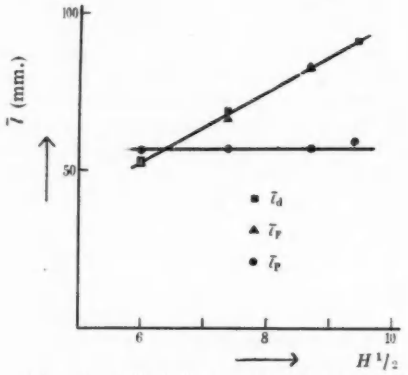

Fig. 6. Effect due to the height of mercury reservoir.
Solution: 10^{-3} M $TlNO_3$ in 0.1 N KCl
ΔE=100mV. Sensitivity of galvanometer is 1/30 for $\bar{i}_d$ and $\bar{i}_F$, and 1/10 for $\bar{i}_q$.

It is clear that the limiting diffusion current of the ordinary polarogram and also that of the Fournier's polarogram are nearly proportional to the square root of the reservoir height. That these two limiting currents must coincide at a sufficiently negative potential, is predicted theoretically by Eqs. (1) and (2). On the contrary, the peak current intensity of Breyer's polarogram remains *constant* independently of the reservoir height. This finding suggests that the a. c. component ought to be proportional to the mean value of the drop surface, as in the case of *kinetic current* investigated by Koutecky and Brdička[9]. This result seems to be comprehensible from the fact that the change of the a. c. component of the electrolytic current is much faster than that of the mercury drop surface.

(4) Dependency of Current Intensity on the Concentration of Depolarizer.—The limiting current in the Fournier's polarogram coincides with that of the classical polarogram at a sufficiently negative potential, provided that the drop time remains unchanged, so that it is proportional to the concentration of depolarizing matter. Also it can be derived from Eq. (5) that the peak current intensity of the Breyer's polarogram must be proportional to the concentration. Experimental results with thallous ion are shown

9) J. Koutecky and R. Brdička, *Collection Czech. Chem. Communs.*, 12, 337 (1947).

in Fig. 7, and it is obvious that when the

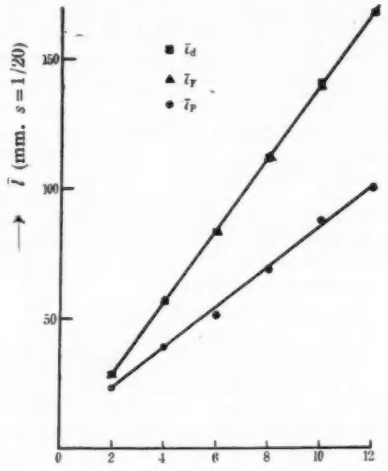

Fig. 7. Dependency of each current intensity on the concentration.
Solution: $TlNO_3$ in 0.1 N KCl. ΔE =80mV.

concentration lies in the concentration range varying from 10^{-4} to 10^{-3} mol. per liter, the satisfactory result is found. Quite the same results are also obtained with cadmium ion. Fig. 8 gives an experimental i_p-$^*C$ curve, in which the bulk concentration $^*C$ of depolarizer is of the order of 10^{-3} molar, and it is found that the peak current approaches to a certain limiting value with the increasing concentration, the phenomenon of which will be discussed later elsewhere.

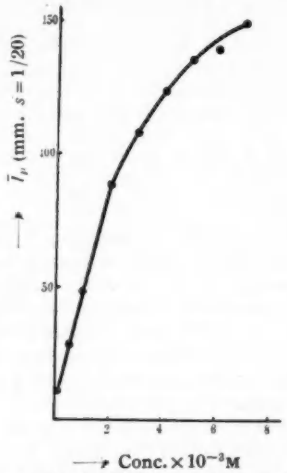

Fig. 8. Dependency of peak current on the concentration.
Solution: $Cd(SO_4)$ in 0.5 N KCl. ΔE =100mV.

Summary

The d. c. and a. c. components of the electrolytic current observed a. c. polarographically, i. e. the Fournier's and Breyer's polarograms, are investigated experimentally for the reversible electro- reductions of cadmium and thallous ions. The result of the experiment shows convincingly the essential legitimacy of our theoretical conclusion.

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*Reactions of Bis-alkylsulfonylmethanes and Their Halogen-substituted Derivatives**)

By Shigeru OAE

(Received June 19, 1954)

Bis-alkylsulfonylmethane is a fairly interesting compound in many respects.[1] Its central methylene group is active like that of dialkyl malonate and behaves quite similarly. For example, methyl iodide reacts with sodium salt of bis-alkylsulfonylmethane according to the following equation.[1,2]

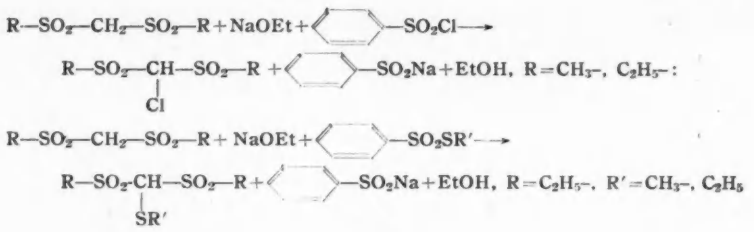
$$R{-}SO_2{-}CH_2{-}SO_2{-}R + NaOEt + CH_3I \longrightarrow R{-}SO_2CH(CH_3){-}SO_2{-}R + NaI + EtOH$$

This active methylene group readily undergoes electrophilic substitution. A few typical reactions of this type are as follows:

* A part of this study was made at the Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.

1) C.M. Suter, "The Organic Chemistry of Sulfur", pp. 739

2) (a) E. Fromm, *Ann.*, **253**, 141 (1889). E. Fromm et al., ibid., **394** 344 (1912).



The former reaction presumably takes place by the attack of chlorine cation, while the latter does by that of SR'. However, no similar reaction was observed between ethyl benzenesulfonate and bis-alkylsulfonylmethane. This mixture eventually did not react under the same condition as for the sulfur analog.

A reaction was carried out between sodium salt of bis-alkylsulfonylmethane and methyl nitrate under the speculation that it might give bis-alkylsulfonyl-methoxymethane. However, the resulting compound was found to be bis-alkylsulfonyl-methylmethane; namely, it would be a simple nucleophilic substitution.

$$R{-}SO_2{\cdot}CH_2{-}SO_2{-}R + NaOEt + CH_3ONO_2 \longrightarrow R{-}SO_2{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}{-}SO_2{-}R + NaONO_2 + EtOH$$

Bis-alkylsulfonylmethane is readily halogenated and forms dihalides.[1,2,3] Both dihalide and monohalide of bis-alkylsulfonylmethane show interesting chemical behaviour. Their halogens are easily replaced by hydrogen giving original bis-alkylsulfonylmethane when attacked by nucleophilic reagents. Bis-alkylsulfonyl-dibromomethane reacts with potassium iodide liberating iodine,[2b] while it reacts with thiophenol giving diphenyldisulfide.[1a] Aqueous ammonia, sodium acetate and potassium thiocyanate also replace bromine by hydrogen. These reactions with bis-alkylsulfonyldibromomethane can be explained when one assumes that it gives a bromocation which readily oxidizes nucleophilic reagents. This assumption is probably valid, because halogens attached to the central methylene group having two adjacent strong electron-attractive sulfonyl groups, do not readily split as halogen anions but do so as cations rather easily.

In this investigation, a few more similar reactions were observed. Bis-ethylsulfonylchloromethane gave bis-ethylsulfonylmethane in the reaction with sodium methylate. Sodium methylate converted bis-alkylsulfonyldichloromethane also to its original bis-alkylsulfonylmethane. Aluminum ethylate caused practically the same reaction with bis-methylsulfonydibromomethane.

A somewhat peculiar reaction of bis-ethylsulfonyldibromomethane was one with silver nitrate in methanol. The reaction took place almost spontaneously, one bromine being lost, and gave bis-ethylsulfonylbromomethane, which did not undergo any further reaction with excess silver nitrate. On the other hand, its chloro-analog, bis-ethylsulfonyldichloromethane, reacted very little, even though it was boiled for ten hours with silver nitrate in ethanol. The very much higher reactivity of the dibromo compound over the dichloro-analog can not be ascribed only to the difference in the polarizability of the relevant bond. Moreover, the cleavage of bromine as anion would be greatly suppressed by the inductive effect of the two strongly electron-attractiing sulfonyl groups. The failure of explanation by the electrical effect led us to seek the alternative one by the steric effect. As was reported previously[4], the steric requirement of the sulfonylmethyl group is of similar bulkiness to that of the neopentyl group. According to the current concept of "Strained Homomorph" by H. C. Brown[5], di-(*tert*-butyl)-methane is sterically strained by ca. 5 kcal.; therefore, its 'Strained Homomorph', bis-alkylsulfonylmethane should also be sterically strained by as much as about 5 kcal. When one bromine is substituted for its methylene, the resulting monobromocompound will have more strain, but the inductive effect of the two strong electron-attractive sulfonyl groups might still overwhelm the steric strain energy, thus rendering the net result the retardation of reactivity. However, when another bromine is introduced, the steric strain of the resulting bis-alkylsulfonyldibromomethane would suddenly jump up to such an extent that the second bromine atom would no longer be held stably at the methylene carbon, in spite of the strong inductive effect of three other

(b) R.E. Stutz and R.L. Shriner, *J. Am. Chem. Soc.*, **55**, 1242 (1933).
R.L. Shriner et al., ibid., **52**, 2068 (1930).
3) D.T. Gibson, *J. Chem. Soc.*, **1931**, 2637.
4) S. Oae, *Waseda Applied Chem. Bull.*, **21**, No. 1, 7 (1952); ibid., No. 2, 8 (1953).
5) H.C. Brown, *J. Am. Chem. Soc.*, **75**, 1, (1953).

electron-attractive substituents attached to it. Since the chlorine atom is smaller than bromine, even the second chlorine atom might possibly be held with quite enough stability at the methylene carbon, thus showing its inertness in the reaction with silver nitrate.

The reaction of bis-alkylsulfonyldibromomethane with aniline and with toluene were investigated under the speculation that it might be used as a mild brominating agent. However, aniline did not react readily while toluene did, giving benzyl bromide in the presence of a small amount of benzoyl peroxide.

Experimental

Bis-ethylsulfonylmethylmercaptomethane and Bis-ethylsulfonylethylmercaptomethane.—1 g. of methyl *p*-toluenethiosulfonate of m.p. 53–4°, which was prepared by the reaction of methyl iodide upon sodium *p*-toluenethiosulfonate, was reacted with 1 g. of bis-ethylsulfonylmethane in 15 ml. of ethanol dissolving 0.1 g. of metalic sodium. The reaction mixtur was boiled on a water bath for seven hours and then was kept at room temperature overnight. After removing ethanol and allowing the residue to soak in hydrochloric acid until it became acidic, colorless crystalline needles were formed which were collected and recrystalized from ethanol-petroleum ether. 0.7 g. of bis-ethylsulfonyl-methylmercaptomethane of m.p. 119–20° was thus obtained in 57% yield. (Found: S, 39.0. Calcd. for $C_5H_{14}S_3O_4$: S, 39.2%).

Bis-ethylsulfonyl-ethylmercaptomethane of m.p. 103–4° was obtained in 62% yield, starting from ethyl *p*-toluenethiosulfonate of m.p. 50–3° with bis-ethylsulfonylmethane as in the previous case and then recrystallization was performed from benzene-petroleum ether. (Found: S. 36.6; Calcd. for $C_7H_{16}S_3O_4$: S, 36.9%).

The Reaction between Bis-methylsulfonylmethane and Ethyl *p*-toluenesulfonate.—0.5 g. of bis-methylsulfonylmethane was dissolved in 10 ml. of ethanol which dissolved 0.05 g. of metallic sodium. Into this solution, 0.6 g. of freshly prepared ethyl *p*-toluenesulfonate of m.p. 29–30° was added and the whole mixture was boiled on a water bath for an hour. After treating the mixture similarly to the case of thio-analog, only the original substances were isolated. Longer heating was found not to be effective in bringing the reaction any further.

The Reaction between Bis-alkylsulfonylmethane and Methyl Nitrate.—1 g. of bis-methylsulfonylmethane was dissolved in 15 ml. of methanol which dissolved 0.05 g. of metallic sodium. Into this solution 0.5 g. of methyl nitrate was added and the mixture was boiled on a water bath for an hour and a half; then crystals formed. These crystals were collected and were found to be sodium nitrate which was identified by the appearance of blue-violet color when treated with a mixture of diphenylamine and sulfuric acid. The residue was diluted with water and the crystals precipitated were collected. Well-dried crystals were recrystallized from benzene and 0.7 g. of colorless crystals of m.p. 120–122° were obtained. This compound was found to be identical to bis-methylsulfonylmethane of m.p. 124° which was authentically prepared from bis-methylsulfonylmethane and methyl iodide. 0.65 g. of bis-ethylsulfonylmethane and 0.25 g. of methyl nitrate were dissolved in 10 ml. of methanol which contained 0.25 g. of potassium hydroxide, and the mixture was treated as in the previous case, and then bis-ethylsulfonyl-methylmethane of m.p. 75° was obtained. This was identified as bis-ethylsulfonylmethylmethane by the mixed melting point with the authentic sample prepared from bis-ethylsulfonylmethane and methyl iodide.

The Reaction of Sodium Methylate upon Bis-ethylsulfonyldibromomethane.—4 g. of bis-ethylsulfonyl-dibromomethane was added in 40 ml. of methanol which dissolved 0.65 g. of metallic sodium and the whole mixture was boiled for an hour, and then methanol was removed. The residue was diluted with water and the crystals formed were washed with ether, then 2 g. of bis-ethylsulfonylmethane of m.p. 102–3° were obtained. Sodium bromide was obtained from the mother liquor.

The Reaction of Sodium Ethylate upon Bis-methylsulfonyl-dibromomethane.—0.5 g. of bis-methylsulfonyl-dibromomethane was reacted in 5 ml. of ethanol with sodium ethylate made from 0.08 g. of metallic sodium, and then 0.2 g. of bis-methylsulfonylmethane were obtained.

The Reaction of Aluminum Ethylate upon Bis-methylsulfonyl-dibromomethane.—1 g. of bis-methylsulfonyl-dibromomethane was mixed with 0.5 g. of freshly prepared aluminum ethylate, the mixture was sealed in a tube, and the tube was heated at 200° for twenty minutes. After the tube was cooled, the contents were poured into water and then 0.3 g. of crystal melting at 140–45° was obtained. This was identical with bis-methylsulfonylmethane.

The Reaction between Bis-ethylsulfonyl-dibromomethane and Silver Nitrate.—When 1 g. of bis-ethylsulfonyl-dibromomethane was placed into 50 ml. of methanol dissolving 0.5 g. of silver nitrate, the whole solution became milky white and the reaction was over in ten minutes. Then it was further heated up to the boiling point and then was cooled. The silver bromide which formed was filtered off and methanol was removed, and then crystals appeared. These crystals were recrystallized and 0.5 g. of colorless compound of m.p. 121° was obtained. This was found to be monobromo compound. The reaction with large excess of silver nitrate also gave the same compound, though it was heated for a longer period. (Found: Br, 30.0; Calcd. for $C_5H_{11}O_4Br$: Br, 30.4%).

When 0.5 g. of this compound was reacted with 0.3 g. of bromine, the dibromo compound of m.p. 131° was obtained almost quantitatively.

The Reaction between Bis-ethylsulfonyl-dichloromethane and Silver Nitrate.—0.5 g. of bis-ethylsulfonyl-dichloromethane and 0.35 g. of silver nitrate were dissolved in 50 ml. of methanol and the solution was boiled for ten hours, but the solution did not become turbid and the starting material was recovered.

The Reaction between Bis-ethylsulfonyl-dibromomethane and Aniline.—1.5 g. of bis-ethylsulfonyl-dibromomethane and 0.5 g. of aniline were dissolved in 40 ml. of benzene and the solution was boiled for 30 minutes. A small portion of crystal was observed at the end of thirty minutes. Heating was continued for additional four hours and benzene was removed, but no crystalline substance was successfully obtained after a serious attempt.

The same amounts of the starting materials were heated in 50% acetic acid for three hours but only the starting materials were isolated.

The Reaction of Bis-ethylsulfonyl-dibromomethane upon Toluene.—5 g. of bis-ethylsulfonyl-dibromomethane was added to 10 ml. of toluene which dissolved 1 g. of benzoyl peroxide and the whole solution was boiled for five hours. Gradually the solution became lachrymatory. After cooling at the end of five hours, a small portion of benzoic acid of m.p. 120–2° formed in the solution. The remaining oil was distilled in vacuo and 1.5 g. of an oil was obtained which boiled at 70–80°/10 mm. This oil was found to be benzyl bromide which was identified by leading it to S-benzylthiouronium bromide.

Summary

Bis-alkylsulfonylmethane did react with alkyl *p*-toluenethiosulfonate giving bis-alkylsulfonyl-alkylmercaptomethane. Bis-alkylsulfonyl-halogenomethane was found to react with metal alkoxide giving original bis-alkylsulfonylmethane. It was also found that bis-alkylsulfonyl-dibromomethane readily reacts with silver nitrate giving the monobromo-compound while its dichloro-analog resists in the same condition.

The mechanisms of these reactions were discussed.

The author is deeply grateful to both Professor M. Murakami at Osaka University and Professor Calvin A. Van der Werf at the University of Kansas who encouraged him all through this study.

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Studies on Unsaturated Organosilicon Compounds. II. Reactions and Properties of Vinyltrimethylsilane*

By Motonori KANAZASHI

(Received June 22, 1954)

In a previous paper,[1] the syntheses of organovinylsilanes and addition of trichlorosilane to the double bond of these compounds were discussed. The present paper reports three types of reactions of vinyltrimethylsilane, that is, addition, cleavage, and polymerization. Vinyltrimethylsilane is of much theoretical interest because it is one of the simplest unsaturated organosilicon compounds and it has a silicon atom directly bonded to the C=C double bond.

Addition Reactions to the Double Bond.[2]—Vinyltrimethylsilane is thought to be one of the monosubstituted ethylenes; thus to this ethylenic double bond many compounds may be added as to ordinary unsaturated organic compounds.

The hydrogenation of unsaturated organosilicon compounds was first reported by Sommer and his coworkers on allyltrimethylsilane[3] and recently on β-styryltrimethylsilane[4] by the same author. These reactions were carried out under hydrogen pressure with Raney nickel catalyst. In the present study vinyltrimethylsilane was found to be easily hydrogenated under normal conditions with platinum oxide as catalyst in glacial acetic acid solution. The catalytic hydrogenation under normal conditions with platinum or palladium catalyst seems to be useful for the analytical determination of the number of unsaturated

*) This work was presented in the 7th. annual meeting of the Chemical Society of Japan in April, 1954, at Tokyo.

1) M. Kanazashi, This Bulletin, **26**, 493 (1953).

2) Most of the experimental results of this section were presented in the 6th. annual meeting of the Chemical Society of Japan in April, 1953.

3) L.H. Sommer, L.J. Tyler and F.C. Whitmore, *J. Am. Chem. Soc.*, **70**, 2872 (1948).

4) L.H. Sommer, D.L. Bailey, G.M. Goldberg, C.E. Buck, T.S. Bye, F.J. Evans and F.C. Whitmore, *J. Am. Chem. Soc.*, **76**, 1613 (1954).

bonds in organosilicon compounds within an error of about 2%.

The addition of halogen to the double bond of vinyltrimethylsilane was reported by the author[2] and very recently by Sommer and his coworkers[4]. It was found that chlorine and bromine easily add to the double bond of vinyltrimethylsilane, as they do in the case of vinyltrichlorosilane,[5,6,7,8] giving α, β-dihalogenoethyltrimethylsilane as reported by Sommer and his coworkers[4]. Especially the addition of bromine was found also to be useful for the analytical determination of the number of unsaturated bonds of organosilicon compounds by normal methods, i.e. reaction of a sample with carbon tetrachloride solution of bromine followed by a back titration with standard solution of sodium thiosulfate.

The addition of hydrogen halides to the double bond of vinylsilanes was first reported by Larsson[9] on vinyltriethylsilane with hydrogen chloride and bromide in the presence of hydroquinone or benzoyl peroxide. In all cases β-halogenoethyltriethylsilanes were obtained contrary to the well known Markownikoff rule. A similar result was obtained by Wagner and his coworkers[8] in the aluminum chloride catalyzed addition of hydrogen chloride to vinyltrichlorosilane. The present author also found this non-Markownikoff addition to vinyltrimethylsilane of hydrogen bromide and of hydrogen iodide in the presence and absence of a peroxide or an antioxidant, and independently from the above two reports. These results were reported orally in April 1953[2] but it was decided to postpone the publication in a journal until more detailed data for discussion of the reaction mechanism had been obtained.

Recently Sommer and others[4] reported the same results on vinyltrimethylsilane with hydrogen bromide in the presence of benzoyl peroxide and with hydrogen iodide. They found that hydrogen bromide did not add to vinyltrimethylsilane in the absence of a peroxide catalyst during a reasonable time. Contrary to this result, in the present study hydrogen bromide added easily to vinyltrimethylsilane in the absence of a peroxide catalyst or in the presence of catechol as an antioxidant, by a slight warming for ten minutes followed by cooling to −70° and saturating with hydrogen bromide.

The β-halogenoethyltrimethylsilanes obtained by these addition reactions were found to be very unstable. β-Iodoethyltrimethylsilane fumed in air and slowly decomposed to give free iodine, and β-bromoethyltrimethylsilane decomposed even at room temperature by a catalytic action of the surface of unglazed porcelain or ground glass, giving trimethylbromosilane and ethylene.

$$(CH_3)_3SiCH_2CH_2Br \longrightarrow (CH_3)_3SiBr+CH_2=CH_2$$

This β-halogen in α, β-dihalogeno-or β-halogeno-ethyltrimethylsilane could be titrated by dilute alkali solution as reported by Sommer and his coworkers[10].

$$(CH_3)_3SiCH_2CH_2X \xrightarrow{OH^-} (CH_3)_3SiOH+CH_2=CH_2+X^-$$

$$(CH_3)_3SiCHXCH_2X \xrightarrow{OH^-} (CH_3)_3SiOH+CH_2=CHX+X^-$$

Cleavage Reaction of Vinyl-Silicon Bond.—The vinyl-silicon bond in vinyltrimethylsilane was cloven by concentrated sulfuric acid giving ethylene and trimethylsilyl sulfate similarly to the allyl-silicon bond in allyltrimethylsilane[3]. But the reaction was slow compared with that of allyltrimethylsilane. In these reactions a proton seems to add to α-carbon leaving a β-carbonium cation, which undergoes cleavage involving electron-release from silicon to the electronically deficient β-carbon. The resulting trimethylsilyl cation unites with sulfate anion.

$$H_2SO_4 \longrightarrow H^+ + HSO_4^-$$

$$(CH_3)_3SiCH=CH_2+H^+ \longrightarrow (CH_3)_3Si-CH_2-CH_2^+$$

$$(CH_3)_3Si-CH_2-CH_2^+ \longrightarrow (CH_3)_3Si^+ + CH_2=CH_2$$

$$2(CH_3)_3Si^+ + SO_4^{--} \longrightarrow [(CH_3)_3Si]_2SO_4.$$

Cleavage of the vinyl-silicon bond was also attempted by methanolic potassium hydroxide. But contrary to allyltrimethylsilane[3], the expected evolution of ethylene as a reaction product was hardly detected, and starting materials were recovered, indicating that almost no reaction had occurred. In this case, the nucleophilic attack on the electropositive silicon is prevented by the mutual action between the trimethylsilyl and the directly bonded C=C double bond as will be discussed later.

Consideration on the Reaction Mechanisms.—At present it is postulated[11] for the mechanism of the ionic addition to the C=C

5) L.H. Sommer, *U.S.P.*, 2,605,273 (1952).
6) C. Tamborski and H.W. Post, *J. Org. Chem.*, 17, 1397 (1952).
7) C.L. Agre and W. Hilling, *J. Am. Chem. Soc.*, 74, 3895, 3899 (1952).
8) G.H. Wagner, D.L. Bailey, A.N. Pines, M.L. Dunham and D.B. McIntire, *Ind. Eng. Chem.*, 45, 367 (1953).
9) E. Larsson, *Trans. Chalmers Univ. Technol.*, No. 115, 25 (1951).
10) L.H. Sommer, E.H. Dorfman, G.M. Goldberg and F.C. Whitmore, *J. Am. Chem. Soc.*, 68, 488 (1946); ibid., 68, 1083 (1946).
11) Dewar, "The Electronic Theory of Organic Chemistry", (1949), p. 143.

double bond that a positive part of the reagent makes a complex with π-electron pair and then combines to electron-rich carbon, forming a carbonium cation which unites with a negative part of the reagent. Both these results of the non-Markownikoff addition of hydrogen halides to vinyltrimethylsilane and cleavage reactions of this compound by concentrated sulfuric acid described above, provide clear evidence for the addition of a proton to α-carbon forming a β-carbonium cation intermediately. This addition of proton to α-carbon is thought to result from electronic polarization of vinyltrimethylsilane as follows.

$$(CH_3)_3Si\overset{\delta-}{-}CH=\overset{\delta+}{C}H_2$$

But such an electronic polarization is inconsistent with an established inductive effect of electron-release, relative to alkyl for trimethylsilyl, Me_3Si[12,13].

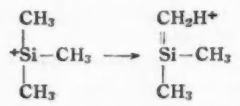
Larsson[9] pointed out the similarity between vinyltriethylsilane and acrylic acid toward hydrogen chloride or bromide. Hydrogen halide adds to α, β-unsaturated carbonyl compounds such as acrylic acid to give β-halogeno-compounds in the absence or presence of a peroxide catalyst. And this is explained by the limit formula of resonance hybrids of these compounds as follows.

$$-CH=CH-C=O \longleftrightarrow -\overset{+}{C}H-CH=C-\overline{\underline{O}}^{-}$$

For the resonance hybrids of vinyl and allyl silicon compounds, the following limit formulae may be considered (left for vinyl and right for allyl compounds).

I	$CH_2=CH-Si$	$CH_2=CH-CH_2-Si$
II	$\dot{C}H_2-\dot{C}H-Si$	$\dot{C}H_2-\dot{C}H-CH_2-Si$
III	$CH_2^+-CH^--Si$	$CH_2^+-CH^--CH_2-Si$
IV	$CH_2^--CH^+-Si$	$CH_2^--CH^+-CH_2-Si$
V	$CH_2=CH^-\ Si^+$	$CH_2=CH-CH_2^-\ Si^+$
VI	$CH_2=CH^+\ Si^-$	$CH_2=CH-CH_2^+\ Si^-$
VII	$CH_2^+-CH=Si^-$	$CH_2=CH^+\ CH_2=Si^-$

Among the last three formulae involving the interaction with silicon atom, V is considered to make a larger contribution to the structures of the compounds than VI, due to the smaller electro-negativity of silicon relative to carbon[14], and a possibility of hyperconjugation of three methyl groups in the resulting trimethylsilyl cation as follows[15].



Further, V seems to make a larger contribution to the structures of allyl compounds than to those of vinyl compounds for its allylic resonance as shown below.

$$CH_2=CH-CH_2^- \longleftrightarrow CH_2^--CH=CH_2$$

VII corresponds to the structures of α, β-unsaturated carbonyl compounds and it is considered that the silicon has the tendency to expand its valence shell by the interaction of the $3d$ orbitals of silicon with π-electrons of C=C double bond and to place ten electrons around it. But this interaction is prevented by the shielding effect of a methylene group between silicon and C=C double bond in allyl silicon compounds, and contribution of VII to the structures of allyl silicon compounds seems therefore to be small.

It is explained by these two structures, i.e. V and VII, that a proton adds to α-or γ-carbon for vinyl or allyl compounds respectively and give β-carbonium cation. It unites with a halogen anion to give β-halogeno-compound as an addition product, or it undergoes cleavage involving electron-release from silicon to electronically deficient β-carbon by the stronger action of the sulfate anion than the halogen anion, then the resulting trimethylsilyl cation unites with sulfate anion to give trimethylsilyl sulfate and ethylene as cleavage products.

In the case of the reaction with potassium hydroxide, the nucleophilic attack on electropositive silicon having a tendency to expand its valence shell is postulated[3]. This nucleophilic attack on silicon is accelerated by structure V, but prevented by structure VII because of the electronegative silicon whose valence shell is already expanded in this structure. It seems to be the reason why vinyltrimethylsilane did not react with methanolic potassium hydroxide contrary to allyltrimethylsilane, because the contribution of V is smaller and that of VII is larger in vinyl than allyl compounds.

Sommer and his coworkers reported that hydrogen chloride added to isopropenyltrimethylsilane to give α-chloroisopropyltrimethylsilane as an addition product[4], and isopropenyltrimethylsilane reacted with concentrated sulfuric acid to give *tert*-butyldimethylsilanol hemi-hydrate after treatment with water, as an intramolecular rearrangement product[16], both indicating addition of

12) H. Gilman and G. E. Dunn, *Chem. Res.*, 52, 77 (1953).

13) (a) L.H. Sommer, J.R. Gold, C.M. Goldberg and N.S. Marans, *J. Am. Chem. Soc.*, 71, 1509 (1949); (b) L.H. Sommer and J. Rockett, ibid., 73, 5130 (1951).

14) Pauling, "The Nature of the Chemical Bond", (1940), p. 58—70.

15) A similar hyperconjugation was proposed by Yakubovich, et. al., (*Uspekhi Khim. S.S.S.R.*, 18, 46 (1949)) to explain the C—Si bond distance in methylchlorosilanes.

16) L.H. Sommer and F.J. Evans, *J. Am. Chem. Soc.*, 76 1030 (1954).

a proton to the terminal methylene group of the olefinic grouping to give α-carbonium cation intermediately. These reactions are explained by considering that a resonance structure such as V or VII is overcome by introduction of a single α-methyl having a possibility of hyperconjugation as follows.

$$CH_2=C(CH_3)-Si \longleftrightarrow {}^{-}CH_2-C(=CH_2H^{+})-Si$$

They reported also that β-chlorovinyltrimethylsilane gave no β-elimination on titration with dilute alkali, in contrast with saturated β-halogenoalkyl compounds[4]. This evidence is explained by considering the resonance structure similar to VII as shown below.

$$Cl-CH=CH-Si \longleftrightarrow {}^{+}Cl=CH-CH=Si^{-}$$

Petrov[17] reported that hydrogen bromide added to isobutenyltrimethylsilane to give β-bromoisobutyltrimethylsilane. This is also explained by considering resonance structrures such as V or VII, and VII is further conjugated with the two methyl groups bonded to β-carbon as follows.

$$(CH_3)_2C=CH-Si \longleftrightarrow (CH_3)_2\overset{-}{C}-\overset{+}{C}H\ Si \longleftrightarrow (H^{+}CH_2)(CH_3)C=CH-\overset{-}{Si}$$

Many reactions of vinyl, allyl and other related organosilicon compounds are able to be explained by the two resonance structures discussed above. These two structures were postulated by several authors[18,19], but Gilman and Dunn[11] considered it unlikely that organosilicon compounds received significant contributions from resonance structures involving silicon-carbon double bond as VII.

Recently the resonance structures involving a silicon-carbon double bond as VII was postulated for nitration of trimethylsilylbenzene by Speier[20] and for Hammett's σ-values of p-trimethylsilyl-phenol, aniline and dimethylaniline by Benkeser and Krysiak[21]. Sommer and his coworkers pointed out this limited non-inductive effect of trimethylsilyl in vinyltrimethylsilane similarly to the consideration in this paper.

Further evidence for this resonance structure was obtained from infrared and Raman spectra of these compounds. Petrov and Nikishin[17] reported on a characteristic absorption band due to the $\nu_{C=C}$ vibrational mode at 1620 cm.$^{-1}$ in the infrared absorption spectra of isobutenyltrimethylsilane, and Egorov and Bazhulin[22] reported on a similar band at 1591 cm.$^{-1}$ for vinyltriethylsilane. In a previous paper[1] it was reported that the characteristic absorption band due to the $\nu_{C=C}$ vibrational mode was found at 6.29–6.30 μ (1590–1587 cm.$^{-1}$) in the infrared spectra of four vinylsilanes, i.e. vinyltrimethylsilane, divinyldimethylsilane, vinyltriethylsilane and vinyldimethylphenylsilane[23]. In the present study, the same band at 1590 cm.$^{-1}$ was also observed with Raman spectrum of vinyltrimethylsilane.

It is postulated that $\nu_{C=C}$ is primarily dependent upon the C=C streching force constant and is therefore lowered by conjugation, showing a shift of $\nu_{C=C}$ from the standard position, ca. 1650 cm.$^{-1}$, to longer wave length[24].

The observed shift of $\nu_{C=C}$ in these vinyl or isobutenyl silanes, provides a clear evidence of the presence of conjugation such as in structure VII in these compounds, as in the case of conjugated nitriles[25], ketones and esters of α, β-unsaturated acids[26]. Studies of the conjugation of vinyltrimethylsilane by electron diffraction and dipole moment measurement are under way.

Polymerization Reactions.—The four vinylsilanes synthesized in a previous study[1] did not seem to be polymerized by heating for twenty four hours at 150° in the presence of benzoyl or acetyl peroxide[2]. (For details see the experimental part of the present paper). It was already reported by Ushakov and Itenberg[27] that vinyltriethylsilane was not polymerized by heating in the presence of a peroxide catalyst.

Recently Wagner and his coworkers[5] reported polymerization of vinyltrichlorosilane and vinyl triethoxysilane at high temperature in the presence and absence of a peroxide

17) A.D. Petrov and G.I. Nikishin, *Doklady Akad. Nauk, S.S.S.R.*, **93**, 1049 (1953).
18) J.D. Roberts, E.A. McElhill and R. Armstrong, *J. Am. Chem. Soc.*, **71**, 2923 (1949).
19) H. Soffer and T. De Vries, ibid., **73**, 5817 (1951).
20) J.S. Speier, ibid., **75**, 2930 (1953).
21) R.A. Benkeser and H.R. Krysiak, ibid., **75**, 2421 (1953).
22) Yu. P. Egorov and P.A. Bazhulin, *Doklady Akad. Nauk S.S.S.R.*, **88**, 647 (1953).
23) The characteristic bands at 9.94—9.99 μ, and 10.50—10.54 μ in the spectra of the four vinylsilanes reported in a previous paper[1], are considered to be assigned to the out-of-plane bending vibrational mode of H in the ethylene group according to the results of Davison and Bates[24].
24) W.H.T. Davison and G.R. Bates, *J. Chem. Soc.*, 1953, 2607.
25) Sheppard and Sutherland, ibid., 1947, 453; Kitson and Griffith, *Anal Chem.*, **24**, 334 (1952).
26) Hartwell, Richards and Thompson, *J. Chem. Soc.*, 1948, 1436.
27) S.N. Uschakow and A.M. Itenberg *Zhr. Obshchei Khim. S.S.S.R.*, **7**, 2495 (1937).

catalyst or a Friedel-Crafts type catalyst such as aluminum chloride. There was obtained a low molecular weight polymer consisting mainly of tetramers, by heating at 290° without a catalyst or by heating 50–90° with a Friedel-Crafts type catalyst. But with a peroxide catalyst the formation of polymer was very small. And a high molecular weight polymer was not obtained in all cases.

In view of the conflicting evidence as to the ability of vinylsilanes to polymerize, it seemed of importance to reinvestigate the subject. In the present study, therefore, the radical polymerization of vinyltrimethylsilane with peroxide or α, α'-azodiisobutyronitrile as a catalyst and the cationoid polymerization of the same compound with a Friedel-Crafts type catalyst were investigated. Contrary to vinyltrichlorosilane, vinyltrimethylsilane gave no polymer by the cationoid polymerization and gave a small amount of low molecular weight polymer by the radical polymerization. No high molecular weight polymer was obtained from vinyltrimethylsilane.

The absence of high molecular weight polymers in the product from vinyltrichloro- or vinyltrimethyl-silane seems to result from the steric hindrance of the large trisubstituted silyl group in the structural unit of the polymer, $-CH_2\underset{\displaystyle SiX_3}{\underset{|}{C}}H_2-$ (X=Cl, Me, Et), as shown in Fig. 1. The presence of a polymer of relatively high molecular weight in the product from vinyltriethoxysilane seems to be explained by the free rotation of the ethoxy group around Si—O bond as shown in Fig. 2.[28]

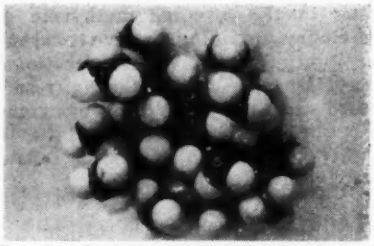


Fig. 1. A growing (pentameric) chain of polymerizing vinyltrimethylsilane. Further addition seems to be very difficult.

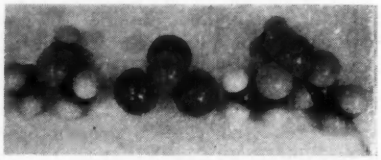


Fig. 2. Comparison of steric effect of tri-substituted silyl group. (left to right: trimethylsilyl, trichlorosilyl and triethoxysilyl group).
The extent of a group bonded to silicon in the neighboring space around silicon is able to be made the smallest in triethoxysilyl by the free rotation of the ethoxy group around Si-O bond.

Further studies on polymerization and other reactions of vinylsilanes are being continued now in this laboratory.

Experimental

Addition Reactions.—Products of addition reactions to the double bond of vinyltrimethylsilane are listed in Table I.

TABLE I

Reagent	Catal.	Product Me_3Si-	Yield %	m.p. °C	b.p. °C	b.p. mm.	d_4^{20}	n_D^{20}	Mol. ref. Calcd.	Mol. ref. Found	Titratable halogen % Calcd.	Titratable halogen % Found
H_2	Pt	CH_2CH_3 a)	70		62–4	760	0.6839	1.3821	34.91	34.80		
Cl_2		$CHClCH_2Cl$ b)	76	−16	67–9	20	1.0586	1.4608	44.59	44.37	20.72	21.2 j)
Br_2		$CHBrCH_2Br$ c)	90	−7	62–3	4	1.5321	1.5062	50.27	50.45	30.73	33.5 j)
$HSiCl_3$	Ac_2O_2	$CH_2CH_2SiCl_3$ d)	90	−18	94–6	50	1.1062	1.4473	57.32	56.96	45.13	45.0
HBr		CH_2CH_2Br e)	65		50–2	21	1.1481	1.4562	42.59	42.91	44.11	44.1
HBr	Ac_2O_2	CH_2CH_2Br e)	72		49	19	1.1489	1.4556	42.59	42.86	44.11	44.6 j)
HBr	Bz_2O_2	CH_2CH_2Br e)			35–45 g)	20	1.1483	1.4560	42.59	42.89	44.11	45.4 j)
HBr	Catechol	CH_2CH_2Br e)			33–47 g)	20	1.150	1.4568	42.59	42.88	44.11	44.5 j)
HI		CH_2CH_2I f)			53–5	10	1.3976	1.4950	47.77	47.61	55.62	57.3 j)

(a) b.p. 62°C (760 mm.), d_4^{20} 0.6849, n_D^{21} 1.3820.[29] (b) b.p. 61°C (14 mm.), d_4^{20} 1.0537, n_D^{20} 1.4617, m.p. −15°C.[4,30] (c) b.p. 74–5°C (8 mm.), d_4^{20} 1.5497, n_D^{20} 1.5095, m.p. −9–11°C.[4] (d) Reported in a previous paper.[1] (e) b.p. 64–5°C (39 mm.), d_4^{20} 1.1499, n_D^{20} 1.4575.[4] (f) b.p. 76–76.5°C (27 mm.), d_4^{20} 1.3862, n_D^{20} 1.5008.[4] (g) Decomposition occurred. (h) To a solution of the sample in methanol, there was added N/5 NaOH aq. solution and back titrated by N/10 HCl with phenol phthalein as an indicator. (i) Calculated for a halogen bonded to β-carbon or silicon. (j) This high halogen value seems to result from decomposition during distillation or preservation.

28) B.A. Arbuzov and T.G. Shavsha, *Doklady Akad. Nauk S.S.S.R.*, **68**, 859 (1949); C. A., **44**, 886 (1950).
29) F.C. Whitmore, L.H. Sommer, et. al., *J. Am. Chem. Soc.*, **68**, 475 (1946).
30) L.H. Sommer, U.S.P., 2,605,273 (1952).

1. Hydrogenation.—A solution of 6.84 g. of vinyltrimethylsilane in 150 cc. of glacial acetic acid was shaken with hydrogen for two hours in the presence of 0.1 g. of platinum oxide catalyst. The absorption of hydrogen took about two hours, being very fast during the middle period of twenty minutes. At the end the volume of absorbed hydrogen was 1444 cc. (including 18 cc. used for reduction of the catalyst), corresponding to 1.013 mole per mole of vinyltrimethylsilane. The reaction product was separated from the catalyst by filtration, then a fraction boiling up to 90° was collected upon fractionation. Twenty grams of toluene was added to the fraction and washed with 10% sodium bicarbonate solution and water. After drying over calcium chloride, the fractionation of the product gave ethyltrimethylsilane as shown in Table I.

2. Halogenation.—Ten grams (0.1 mol.) of vinyltrimethylsilane was cooled to −70° in a bath of dry ice and acetone, then a theoretical amount of bromine was added drop by drop or a theoretical amount (from weight increase) of chlorine was bubbled with shaking. Toward the end of the reaction white crystals of the product were observed. Upon warming to room temperature, the product was fractionated and α, β-dibromo- or dichloro-ethyltrimethylsilane was obtained as shown in Table I.

3. Addition of Hydrogen Bromide.—In a test-tube equipped with gas inlet and outlet tubes, there was placed 10 g. (0.1 mol.) of vinyltrimethylsilane. Hydrogen bromide gas dried with phosphorus pentoxide was introduced in the first experiment, but 0.1 g. of peroxide or catechol was added prior to the introduction of HBr in the other three experiments. The reaction mixture was warmed slightly for ten minutes to initiate the reaction and cooled to −70° in a bath of dry ice and acetone, then saturated with a theoretical amount of HBr. Standing overnight up to room temperature, the reaction mixture was fractionated giving β-bromoethyltrimethylsilane as shown in Table I.

Decomposition of β-Bromoethyltrimethylsilane.—The β-bromoethyltrimethylsilane thus obtained was very unstable and decomposed by slight heating in distillation or other treatment, and with a catalytic action of a surface of unglazed porcelain or ground glass it decomposed even at room temperature. In a flask fitted with a reflux condenser and a gas outlet tube at the top, containing a few small pieces of unglazed porcelain such as boiling chips, there was added β-bromoethyltrimethylsilane. At once a vigorous reaction occurred and almost half of the sample was lost. Then the remaining liquid was heated slowly on a water bath, a reaction occurred at 40–45°, and ethylene gas was evolved. Ethylene was identified by convertion to ethylene dibromide, n_D^{15} 1.5392. The residue was fractionated and trimethylbromosilane boiling at 80.5–81.0° was obtained, this was converted to disiloxane, n_D^{17} 1.3784.

4. Addition of Hydrogen Iodide.—In a test-tube equipped with gas inlet and outlet tubes, there was placed 10 g. (0.1 mol.) of vinyltrimethylsilane. Hydrogen iodide gas dried with phosphorus pentoxide was introduced in the test-tube cooled to −30° in a bath of dry ice and acetone. After a theoretical increase in weight had taken place, the reaction mixture was allowed to be warmed slowly to room temperature and it was fractionated, giving β-iodoethyltrimethylsilane as shown in Table I.

Cleavage Reactions 1. With Concentrated Sulfuric Acid.—In a test-tube equipped with a gas outlet tube, there was placed 3 g. of vinyltrimethylsilane and 1.5 g. of conc. H_2SO_4 and cooled to −20° in a bath of dry ice and acetone. But almost no reaction occurred at this temperature. Then the reaction mixture was warmed to room temperature (15–20°) with shaking, the reaction proceeding slowly with the evolution of ethylene gas. The ethylene was absorbed by carbon tetrachloride solution of bromine. The reaction became rapid gradually, and the upper layer of vinyltrimethylsilane decreased, while the lower layer of sulfuric acid increased conversely. The reaction became more and more vigorous and the temperature rose to about 40° in the course of four hours, toward the end of which the reaction mixture became homogeneous. It was cooled to 10° and gradually warmed up to 20°. After about six hours the reaction came to the end and no more ethylene was evolved. The carbon tetrachloride solution was fractionated and 3 g. of ethylene dibromide was obtained, n_D^{15} 1.5410 (after washing with H_2O and drying with $CaCl_2$), about 50% yield. The residue was solidified by cooling and melted at 46–51°; it therefore seems to be crude trimethylsilyl sulfate, of which the melting point of a pure specimen is reported to be 56–58°[31].

2. With Methanolic Potassium Hydroxide.—In a 50 cc. flask equipped with a reflux condenser and a gas outlet tube at the top, there were placed 10 g. (0.1 mol.) of vinyltrimethylsilane, 12 g. (ca. 0.2 mol.) of KOH and 10 g. of methanol. The mixture was heated at the reflux temperature for 15 hrs., but the evolution of a gaseous product was hardly detected. The reaction mixture was distilled rapidly at a reduced pressure. Upon fractionation of the distillate, 9.5 g. of an azeotrope of methanol and vinyltrimethylsilane, b.p. 44.3° n_D^{20} 1.3865, and a mixture of methanol and vinyltrimethylsilane, b.p. 46–60°, n_D^{20} 1.3350, were obtained. Neither trimethylmethoxysilane (in an azeotrope with methanol) nor trimethylsilanol was obtained. The azeotrope was further characterized by an independent preparation as follows. A mixture of 5 g. of vinyltrimethylsilane and 5 g. of methanol was distilled through a distillation column of about 10 theoretical plates. A fraction boiling at 44.3°, n_D^{20} 1.3860 was obtained, but the ratio of

31) L.H. Sommer, et. al., *J. Am. Chem. Soc.*, **68**, 156 (1946). Sommer, et. al.[9] reported m.p. 49—52° for a crude one.

two components was not determined.

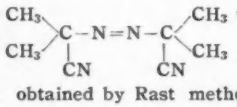
Polymerization Reactions 1. Polymerization of vinylsilanes on a small scale.—A half gram of each three vinylsilanes, i.e. trimethylvinylsilane, dimethyldivinylsilane, and dimethylphenylvinylsilane, was heated at 100° or 150° for 24 hours in a sealed glass tube in the presence of 10 mg. of acetyl or benzoyl peroxide. But neither solidification nor increase of viscosity was found even in the case of divinyldimethylsilane, indicating that no polymerization occurred.

2. Polymerization of Vinyltrimethylsilane.—The conditions of polymerization of vinyltrimethylsilane and properties of the polymers are shown in Table II.

TABLE II

POLYMERIZATION OF VINYLTRIMETHYLSILANE

Catalyst	Yield %	Polymer Fraction	B.p. °C.	B.p. mm.	n_D^{20}	Mol.[c] Weight	Analytical Data C% Calcd.[d]	C% Found	H% Calcd.[d]	H% Found
Bz_2O_2-Ac_2O_2	15	I.	100–104	8–9	1.4593	360	59.91	61.20	12.07	11.86
		II.	120–140	3	1.4698	460	59.91	61.12	12.07	11.69
		residue			1.4780	550	59.91	60.25	12.07	11.76
Azonitrile[a]	10	I.	80–100	3–10	1.4474	400	59.91	61.01	12.07	11.73
		II.	100–130	2	1.4568	350	59.91	63.63	12.07	12.07
		residue			1.4763	1000				
$AlCl_3$	2									
BF_3[b]	0									

a) α, α'-Azodiisobutyronitrile  was used. b) used as an addition compound with diethylether. c) obtained by Rast method, but these values are very rough. d) calculated for $(C_5H_{12}Si)n$

With Acetyl Peroxide and Benzoyl Peroxide Mixture.—In a sealed glass tube there were placed 20 g. (0.2 mol.) of vinyltrimethylsilane, 0.12 g. (0.5 mol.%) of diacetyl peroxide, and 0.24 g. (0.5 mol.%) of dibenzoyl peroxide. The tube heated at 150–5° for 24 hours. Unreacted vinyltrimethylsilane was recovered at atmospheric pressure. The precipitated crystals of benzoic acid were filtered, recrystalized, m.p. 117–8°, mixed m.p. to be 117.5–9.0°. The filtrate was fractionated under reduced pressure to give fractions as shown in Table II.

With Other Catalysts.—Similarly to the case with the peroxide catalyst, all catalyst were used in amount of 1 mole % to vinylsilanes. But heating at 150° for boron trifluoride and 120° for α, α'-azodiisobutyronitrile and aluminum chloride was employed. As in the case of azonitrile, tetramethylsuccinonitrile was isolated as a decomposition product of the catalyst, m.p. 165.5–6.5°, mixed m.p. 165.5–7.0°. In the case with boron trifluoride and aluminum chloride almost no polymer was obtained.

Summary

1) Addition reactions to the double bond of vinyltrimethylsilane were studied with hydrogen, bromine, chlorine, hydrogen bromide and iodide, and the properties of the products were given.

2) Vinyl-silicon bond was cloven by concentrated sulfuric acid but no reaction occurred with methanolic potassium hydroxide.

3) Reaction mechanisms of the above two reactions of vinyl, allyl or related unsaturated organosilicon compounds were discussed. A conjugated structure involving silicon-carbon double bond in which the silicon atom has an expanded valence shell was postulated for some of these reactions. Such a structure was further confirmed by the shift of $\nu_{C=C}$ in the absorption spectra of vinyltrimethylsilane.

4) Polymerization reactions of this compound were studied and the steric hindrance by a large trimethylsilyl group in the structural unit of the polymer was discussed, particularly concerning the absence of a high molecular weight polymer in the reaction product.

The author wishes to express his sincere thanks to Dr. O. Simamura and Dr. T. Yamada for their kind advice and encouragement during this work. The author is also indebted to Mr. I. Tsuchiya for the Raman spectra reported in this paper and to Mr. M. Takakusa for his assistance during this work.

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*Influence of the Addition of High Molecular Electrolyte upon the Absorption Spectra and Fluorescence of Organic Dyestuffs. IV.**

By Noboru MATAGA and Masao KOIZUMI

(Received July 19, 1954)

Introduction

In the earlier papers[1,2,3] of this series, the present authors have investigated the influence of the addition of high molecular electrolyte upon the absorption spectra and fluorescence of basic dyes. The conclusion then reached was that for the interpretation of metachromasy, the change of aggregation of dye ions caused by the addition of high molecular electrolyte is of primary importance rather than the direct interaction between dye and high molecular electrolyte.

Now, an investigation has been made with acidic dyes which, in contrast to basic dyes, have little tendency to associate in the aqueous solution and accordingly obey Beer's law quite well. The influence upon absorption spectra and fluorescence of such dyes caused by the addition of basic electrolytes of various molecular weights was examined in order to confirm our previous conclusion more definitely.

The acidic dyes examined were uranine, eosine and erythrosine, and the following basic electrolytes were used: a) chitosan hydrochloride b) glucosamine hydrochloride and c) several aliphatic amines of different chain length.

As the result of the investigation using various combinations of dyes and electrolytes, it was found that the data can be interpreted along the same reasoning as before, and the phenomenological interrelation has now become more comprehensive.

The present paper reports in a rather abbreviated form some experimental results and the discussions based upon them. The details will be published in J. Inst. Polytech. Osaka City Univ.

Experimental Results

Beckman spectrophotometer model D.U. was used for the measurement of absorption spectra and the relative intensities of the fluorescence.

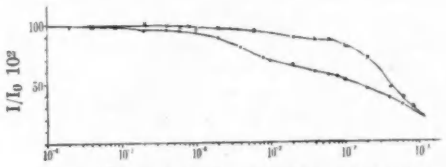
Sample.—Uranine (Merck) was purified by recrystallisation.

Glubler's eosine and erythrosine were used without further purification.

Chitosan hydrochloride and glucosamine hydrochloride were kindly supplied by Mr Kanji Okawa of the Institute of Cellulose Research of Osaka University.

Methylamine hydrochloride is of commercial supply, *n*-propylamine and *n*-dodecylamine hydrochloride were kindly supplied respectively by Mr. Shiro Morimoto and Shuji Saito of Osaka University.

1) Uranine *a) Chitosan hydrochloride.*—The absorption spectra and the relative intensity of fluorescence of the aqueous uranine solution containing various quantities of chitosan hydrochloride, are shown in Figs. 1 a and 2, respectively.



a. Chitosane hydrochloride (mol./*l.*) (log scale)
b. Glucosamine hydrochloride (mol./*l.*) (log scale)

Fig. 1. Change of relative fluorescence intensity of aqueous uranine solution by added chitosan hydrochloride, and glucosamine hydrochloride. Dye conc., 2×10^{-5}mol./*l*; temperature, 27°C.
○ a
× b

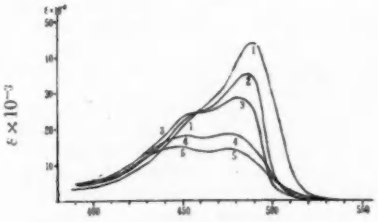


Fig. 2. Change of absorption spectrum of aqueous uranine solution by chitosane hydrochloride.
Dye conc. 2×10^{-5}mol./*l*. Temperature, 27°C. Quantity of added chitosane hydrochloride: (1) 0–4×10^{-5}mol./*l*. (2) 6×10^{-5} mol./*l* (3) 8×10^{-5}mol./*l*. (4) 6×10^{-4}mol./*l*. (5) 2×10^{-3}mol./*l*.

* Physicochemical Studies of Organic Dyestuffs in Relation to Photochemistry. VI.

1) M. Koizumi and N. Mataga, This Bulletin, **26**, 115 (1952).
2) M. Koizumi and N. Mataga, ibid., **27**, 194 (1954).
3) N. Mataga and M. Koizumi, ibid., **27**, 197 (1954).

Up to 10^{-5} mol./*l*. (referred to a unit group with one amino group) of the added chitosan hydrochloride, no change is observed.

In the range between -10^{-5} and -10^{-4} mol./*l*., the intensity of fluorescence slightly decreases, while the absorption spectra change conspicuously in such a manner as to suggest the existence of an association equilibrium of some kind between chitosan hydrochloride and uranine.

Beyond 10^{-4} mol./*l*., quenching of fluorescence gradually increases and at the same time the intensity of absorption wholly decreases.

There is observed no phenomenon of recovery either in fluorescence or absorption, however much chitosan hydrochloride is added.

b) Glucosamine hydrochloride.—The variations of the relative fluorescence intensity and the change of absorption spectra when various quantities of glucosamine hydrochloride (a structural unit of chitosan hydrochloride) are added to the uranine solution, are shown in Figs. 1 b and 3.

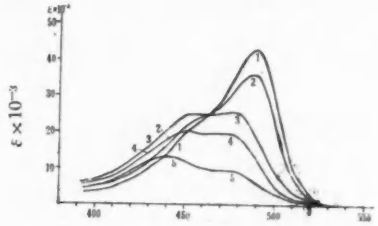


Fig. 3. Change of absorption spectrum of aqueous uranine solution by glucosamine hydrochloride.
Dye conc. 2×10^{-5}mol./*l*. Temperature 27°C. Quantity of added glucosamine hydrochloride (1) 0～10^{-4}mol./*l*. (2) 6×10^{-4}mol./*l*. (3) 6×10^{-3}mol./*l*. (4) 2×10^{-2} mol./*l*. (5) 6×10^{-2}mol/l.

Up to 10^{-4} mol./*l*., there scarcely exists any change either in fluorescence intensity or absorption spectra.

Between ca. 2×10^{-4} mol./*l*. and ca. 10^{-2} mol./*l*., a slight decrease of fluorescence intensity is observed and quite similar changes of absorption spectra as those observed in the case of chitosan hydrochloride take place.

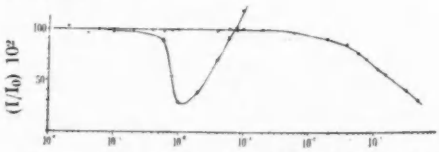
Beyond 10^{-2} mol./*l*., the intensity of fluorescence falls conspicuously and at the same time, the absorption spectra decline in the whole range of visible region. No phenomenon of recovery exists either in fluorescence or absorption.

c) Aliphatic amino compounds.—Only the result of methylamine will be described as a representative.

As small an addition as 2×10^{-5} mol./*l*. causes a rapid increase in the intensity of absorption and from this region up to 10^{-1} mol./*l*. There exists a change of absorption spectra suggestive of an association equilibrium of some kind. No change of fluorescence intensity is observed.

Above 10^{-1} mol./*l*. both the intensity of fluorescence and absorption decreases quite remarkably, and the feature of this decrease is somwhat similar to the case of glucosamine hydrochloride.

2) Eosine and Erythrosine *a) Chitosan hydrochloride.*—The relative intensities of fluorescence and the absorption spectra when various quantities of chitosan hydrochloride are added to the aqueous solution of eosine, are shown in Figs. 4 b and 5.



a. Glucosamine hydrochloride (mol./*l*.) (log scale).
b. Chitosan hydrochloride (mol./*l*.) (log scale).

Fig. 4. Change of relative fluorescence intensity of aqueous eosine solution by added chitosane hydrochloride and glucosamine hydrochloride. Dye conc. 10^{-5}mol./*l*. Temperature, 27°C.
○ a
× b

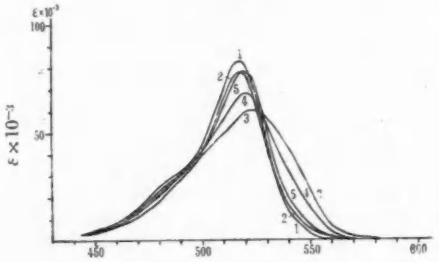


Fig. 5. Change of absorption spectrum of aqueous eosine solution by chitosane hydrochloride.
Dye conc. 10^{-5}mol./*l*. Temperature, 27°C. Quantity of added chitosane hydrochloride. (1) 0～10^{-5}mol./*l*. (2) 6×10^{-5}mol./*l*. (3) 10^{-4}mol./*l*. (4) 4×10^{-4}mol./*l*. (5) 10^{-3} mol./*l*.

There occurs no change either in absorption or fluorescence untill the concentration of chitosan hydrochloride reaches about 10^{-5} mol./*l*.

Beyond this concentration, the fluorescence is quenched gradually and the absorption spectrum shifts toward red and somewhat broadens accompanied with the decrease of extinction.

Such a change becomes most prominent near 10^{-4} mol./*l*., but over this point a marked phenomenon of recovery comes to be observed both in absorption and fluorescence and when the concentration reaches 10^{-3} mol./*l*., the shape of the absorption curve becomes quite similar to that in the pure aqueous solution and the intensity of fluorescence exceeds to some extent, that of the pure aqueous solution.

In the case of erythrosine, the main features

of change of absorption spectra caused by the addition of chitosan hydrochloride, are quite similar as in the case of eosine.

b) Glucosamine hydrochloride.—The effects of glucosamine hydrochloride upon the relative intensity of fluorescence and absorption spectra of the aqueous eosine solution are shown in Figs. 4 a and 6.

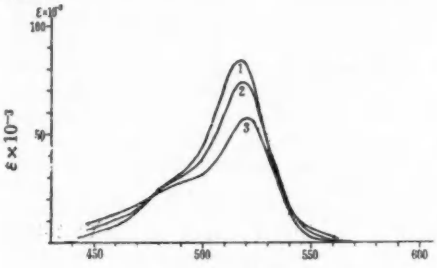


Fig. 6. Change of absorption spectrum of aqueous eosine solution by glucosamine hydrochloride.
Dye conc. 10^{-5}mol./*l.*, Temp, 27°C. Quantity of added glucosaminehydrochloride.
(1) $0{\cdot}6\times10^{-3}$mol./*l.*, (2) 8×10^{-2}mol./*l.*, (3) 3.36×10^{-1}mol./*l.*

No marked change is observed either in fluorescence or absorption below 10^{-2} mol./*l.*, but over this point the intensity of fluorescence gradually falls and the absorption also declines in the whole range.

Quite similar results were obtained for the absorption spectra of erythrosine.

c) Aliphatic amino compounds.—When methylamino hydrochloride is added to the aqueous eosine solution, there is no marked change either in fluorescence or absorption until the concentration reaches as much as ca. 4×10^{-1} mol./*l.*, beyond which the intensity of fluorescence gradually falls accompanied with the decline of extinction in the entire region. The state of affairs for erythrosine is quite similar to eosine.

But in the case of dodecylamine hydrochloride, which is capable of forming micelle[4], quite different phenomena were observed, the changes both in fluorescence intensity and absorption curve are analogous to the case in which alkyl sulfate of long chain is added to basic dyes.

Discussion

It can safely be concluded from the above results, that in the case of uranine there exists no action specific to high molecular electrolyte and the effects of the added electrolyte upon fluorescence and absorption are mainly due to the direct interaction between amino group and dye ion, most probably the ionic association.

Indeed, there is some difference between the effect of aliphatic amine and glucosamine or chitosan hydrochloride, but this is quite natural in view of the fact that aliphatic and ring compounds generally differ much in the property.

It may be worth adding here that in the case of uranine, the fluorescing power is not affected much by its association with amino group, since there is no marked change of intensity in the region where absorption spectra conspicuously change.

Now the state of affairs is quite different in the case of eosine and erythrosine; when the amino compounds of low molecular weight such as methylamine and glucosamine hydrochloride are added to the solution, no change suggestive of strong interaction between amino group and dye ion is perceived at all. Therefore, only a weak interaction due to ionic interaction or van der Waals' force will exist in this case. The conspicuous change of absorption and fluorescence intensity observed in the case of chitosan hydrochloride must accordingly be attributed to the specificity of high molecular substance. The intense quenching of fluorescence by dodecylamine and the phenomenon of recovery occurring prior to micelle formation must also be due to the same reason.

For the interpretation of these phenomena, it is quite natural to adopt the same reasoning as that used in the case of basic dyes; thus they are ascribed to the accumulation of dye ions around high molecular ions by virtue of the weak interaction between them. For example, quenching is produced by the increase of concentration of dye ions around high molecular electrolyte, while the recovery takes place because the accumulation of dye ions around high molecular electrolyte becomes less marked as the latter is increased. In fact, the concentration quenching of the pure aqueous solution of eosine was examined and found to be quite remarkable. The above explanation as it runs, is completely analogous to that applied to the similar phenomena observed when high molecular acidic electrolytes are added to basic dyes. It is an interesting problem to be settled why the interaction of amino group and dye ion is so strong in case of uranine while it is rather weak in eosine and erythrosine; perhaps steric hindrance due to Br and I would be an important factor for it, though the question must of course await further investigations.

Another important result obtained, which shows a sharp contrast to basic dyes, is that no such band as deserves to be called a metachromasy band appears in eosine-chitosan

4) M.L. Corrin and W.D. Harkins, *J. Chem. Phys.*, 14, 641 (1946).

hydrochloride, in spite of the marked accumulation of dye ions around high molecular electrolyte.

One cannot but attribute this difference to the fact that acidic dyes have scarcely any tendency to associate while basic dyes easily dimerise or polymerise. Thus our previous conclusion[1,2,3] that the phenomenon of metachromasy is mainly due to the change of aggregation of dye, conforms quite well with the present results. One may rather say that metachromasy is the conspicuous change of absorption spectra produced by the change of aggregation of dye ions accumulated around high molecular electrolyte when the interaction between dye and functional group of electrolyte is moderate.

Summary

The relative intensity of fluorescence and the change of absorption spectra were examined when chitosan hydrochloride and other amine hydrochloride were added to the aqueous solution of uranine, eosine and erythrosine, which are all acidic and have no tendency to associate.

It was found that in the case of uranine, the interaction between amino group and the dye ion is so strong that it directly influences the absorption band remarkably, and thence the interaction is commonly observed irrespective of whether the molecular weight of electrolyte is high or low. In the case of eosine and erythrosine there exists no such strong interaction between amino group and dye ion because the amino compound of low molecular weight produces no marked change in either fluorescence or absorption; a quite notable change is observed in the case of the amino compounds of high molecular weight; thus for example, the fluorescence at first drops and then recovers as the concentration is increased. The phenomena were interpreted as due to the concentration effect of dye ions gathered around the electrolyte ion by weak attraction. This interpretation is quite analogous to that already applied for basic dyes.

There appeared, however, no metachromasy band and this was ascribed to the fact that the acidic dyes have scarcely any tendency to associate; thus our opinion put forth for the case of basic dyes, that the change of aggregation of dye ions is mainly responsible for metachromasy, was confirmed once more in the case of acidic dyes.

The authors express their hearty thanks to Mr. Okawa, Mr. Morimoto, and Mr. Saito, who gave them the valuable sample. A part of the experiment was done by Mr. S. Oi to whom the authors' thanks are also due.

A part of the expense has been defrayed from a grant by the Ministry of Education.

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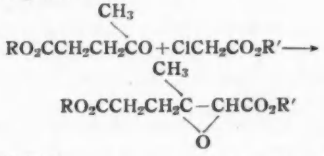
New Derivatives of Levulinic Acid. I.[1] *Synthesis of 2,3-Epoxy-3-Methyladipic Esters*

By Eturô MAEKAWA, Masako MIZOGUCHI* and Yoshio ISHII

(Received August 21, 1954)

Glycidic esters, namely 2, 3-epoxy esters, are easily obtained by the condensation of carbonyl compounds with α-halo esters[2]. Many types of ketones have been reported to give good yields smoothly. Nevertheless, previous investigations of analogous reactions of keto-esters have not been extended beyond the synthesis of γ-lactones by zinc from ethyl levulinate[3] and 3, 3-dimethyllevulinate[4] with ethyl monobromoacetate.

This investigation was undertaken to synthesize glycidic esters, viz. 2, 3-epoxy-3-methyladipic esters, from levulinic and monochloroacetic esters as represented in the following equation:



1) Presented at the 7th Annual Meeting of the Chemical Society of Japan, Tokyo, April 2, 1954.

2) M. S. Newman, *Org. Reactions*, **5**, 413 (1949), a review.

3) H. E. Baumgarten, *J. Am. Chem. Soc.*, **75**, 979 (1953).

4) H. E. Baumgarten and W. P. Schneider, *J. Org. Chem.*, **16**, 1658 (1951).

n-Butyl (I), 2-ethylhexyl and lauryl levulinates were used as a carbonyl component, *n*-butyl (I'), 2-ethylhexyl and lauryl monochloroacetates as halo ester, and sodium methoxide, sodium ethoxide, potassium *tert.*-butoxide[5] and sodium amide as a condensing agent. The synthesis of these glycidic esters was conducted by a slightly modified procedure of the standard Darzens glycidic synthesis.

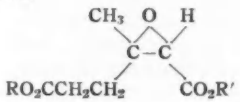
The results are presented in Table I. On the basis of the saponification value and quantitative elemental analysis, it seems reasonable to assume that the products, obtained by the use of potassium *tert.*-butoxide and sodium amide as the condensing agent, are the desired 2, 3-epoxy-3-methyladipic esters, which have not yet been reported in literature. In the case of these two di-*n*-butyl esters, the observed values of molecular refraction are higher by about 0.7 than the calculated value. From consideration of the case of cyclopropane (exaltation is known as +0.7) this exaltation seems to be attributed to the existence of a three-membered oxirane ring neighbouring a carboxyl group.

The epoxy contents of these glycidic esters were determined by Swern's method[6]. The observed epoxy contents of these epoxy esters, however, were about one third of the calculated values, while the observed epoxy content of 2, 3-epoxylauric acid[7] and the observed iodine values for 2, 3-unsaturated acids show also similar results. Therefore the low observed values are probably due to some effect of the neighbouring carboxyl group.

Slight differences are observed between the properties of the two di-*n*-butyl esters, obtained by potassium *tert.*-butoxide and sodium amide respectively, while the esters obtained by sodium amide have a tendency to turn yellow if kept. Therefore these differences may be due to some impurities

TABLE I

2, 3-Epoxy-3-methyladipates



R	R'	Condensing agent	Yield %	b. p.	S. V. Calcd.	S. V. Found	n_D^{20}	Analytical C% Calcd.	Analytical C% Found	Analytical H% Calcd.	Analytical H% Found
n-Butyl	*n*-Butyl	$NaNH_2$	17	148-149°/1.5 mmHg	391.8	395.9	1.4478	62.91	62.80	9.15	9.20
„	„	*tert.*-BuOK	48	189-191°/15 mmHg	„	389.1	1.4458	„	62.56	„	9.25
„	2-Ethylhexyl	$NaNH_2$	(11)	163-165°/1 mmHg	327.6	322.2	1.4537	66.63	66.50	10.01	10.10
2-Ethylhexyl	*n*-Butyl	„	(10)	159°/1 mmHg	327.6	322.5	1.4532	66.63	66.80	10.01	10.15
„	2-Ethylhexyl	„	(8)	ca. 160°/0.1 mmHg	281.5	285.0	1.4599	69.31	69.01	10.62	10.66
n-Butyl	Lauryl	„	(24)	ca. 190°/0.1 mmHg	281.5	288.2	1.4602	69.31	69.27	10.62	10.73
Lauryl	*n*-Butyl	„	(23)	ca. 195°/0.1 mmHg	281.5	273.1	1.4595	69.31	69.20	10.62	10.55
2-Ethylhexyl	Lauryl	„	(25)	ca. 200°/0.1 mmHg	246.8	246.2	1.4650	71.32	71.09	11.09	11.25
Lauryl	2-Ethylhexyl	„	(23)	ca. 200°/0.1 mmHg	246.8	243.0	1.4642	71.32	71.38	11.09	11.30
„	Lauryl	„	(28)	ca. 220°/0.1 mmHg	219.5	225.0	1.4708	72.89	72.75	11.45	11.68
„	„	*tert.*-BuOK	(34)	ca. 220°/0.1 mmHg	„	221.5	1.4695	„	72.70	„	11.58

Yields in parentheses show those of the crude ester.

5) W. S. Johnson, J. S. Belcew, L. J. Chinn and R. H. Hunt, *J. Am. Chem. Soc.*, **75**, 4995 (1953).

*) Present address, Nagoya University, Faculty of Engineering.

6) D. Swern, T. W. Findley, G. N. Billen and J. T. Scanlan, *Anal. Chem.*, **19**, 414 (1947).

7) Unpublished data, 2,3-epoxylauric acid was obtained by epoxidation of *trans*-2-dodecenoic acid with hydrogen peroxide and acetic acid, m.p. 48—48.5°C.

which must be included in the esters by sodium amide[8].

Only a few drops of the pure esters were obtained from the combinations of the higher starting esters, because of their higher boiling points and greater tendency to decompose at elevated temperatures. Also, as commercial sodium amide from different stock was used in each reaction, it is impossible to compare the reactions in regard to yield. But combinations of the lower starting esters gave generally lower yields, which is perhaps due to hydrolysis of the keto-esters. While it was reported that cyclohexanone and monochloroacetic esters gave as high as 90% of the desired products by the use of potassium *tert.*-butoxide[5], only 48% of the desired di-*n*-butyl 2, 3-epoxy-3-methyladipate was obtained from (I) and (I′) under similar conditions. But this yield is still higher than those obtained in the case when sodium amide was used. Sodium ethoxide and methoxide were not suitable as condensing agent, because they probably caused transesterification and gave no desired results. Calculated saponification values are 391.8 for di-*n*-butyl 2, 3-epoxy-3-methyladipate, 488 for the diethyl ester and 555 for the dimethyl ester, while the observed values were 554 for the ester obtained by sodium ethoxide and 585 for the ester obtained by sodium methoxide. Therefore it is deduced that these fractions suffered transesterification and some hydrolysis, and that they were also contaminated by some by-products.

As they are the esters of a dibasic acid and have an epoxy ring, these esters would be able to be utilized as a plasticizer and simultaneously as a stabilizer for polyvinyl chloride (PVC). In fact they showed more excellent results than dioctyl phthalate in our preliminary examinations. For example, the testing sheets, obtained by adding 30, 40 and 50 parts of di-*n*-butyl 2, 3-epoxy-3-methyladipate to 100 parts of polyvinyl chloride, were put to the Shopper tensile strength test at 25°C, and the values of tensile strength, elongation, elongation at 100 kg./cm² load, 100% modulus, tear resistance and permanent set are listed in Table II. Also it was shown that they were heat-proof stabilizers.

TABLE II

SHOPPER TENSILE STRENGTH TEST (at 25°C)

Proportion of the di-*n*-butyl ester (Parts to 100 parts of PVC)	30	40	50
Elongation %	175	245	283
Tensile strength kg./cm²	324	209	206
Elongation at 100 kg./cm² load	5	105	165
100 % Modulus kg./cm²	246	98	68
Tear resistance kg./cm²	161	100	70
Permanent set %	65	12.5	10

Experimental

Reagents. *Levulinic acid.*—This material was obtained by courtesy of the Aji-no-moto Co. Ltd., and was used without purification.

Monochloroacetic acid and sodium amide.—Commercial products were used without purification.

2-Ethylhexyl alcohol.—A commercial product, obtained by courtesy of the Shin-Nihon-Chisso-Hiryo K. K., was distilled under diminished pressure, b. p. 94°C/27 mm Hg.

Lauryl alcohol.—Commercial fatty alcohol, obtained by hydrogenation of coconut oil, was rectified repeatedly in vacuo, b. p. 140–141°C/15mm Hg, hydroxyl value 296.5 (calcd. for $C_{12}H_{25}OH$ 301.1), S. V. 2.5.

tert-Butyl alcohol.—Commercial *tert.*-butyl alcohol was dried by refluxing with sodium and then by distilling in the presence of the free metal[9].

Sodium alcoholates.—Eighteen grams (0.8 mol.) of fresh sodium was dissolved in 450 ml. of anhydrous ethyl or methyl alcohol. Upon removal of the excess alcohol under diminished pressure on a water bath the alcoholate was obtained in the form of yellow or white powder.

Potassium tert-butoxide.—Fresh potassium (5.88 g., 0.15 mol.) was dissolved in 125 ml. of dry *tert.*-butyl alcohol by refluxing in an atmosphere of dry nitrogen[9].

Monochloroacetic and levulinic esters.—*n*-Butyl, 2-ethylhexyl and lauryl esters of these two acids were prepared by refluxing a mixture of an appropriate alcohol, acid and concentrated sulfuric acid with azeotropic removal of water. For the preparation of both the lauryl esters and 2-ethylhexyl levulinate benzene was added to the refluxing mixture. Some properties of these six esters are listed in Table III.

TABLE III

STARTING ESTERS

Ester	b. p.	n_D^{25}	S. V. Calcd.	S. V. Found
Butyl levulinate	125–126°/20 mmHg	1.4257	327.9	325.8
2-Ethylhexyl levulinate	157–159°/15 mmHg	1.4372	245.8	247.6
Lauryl levulinate	190–195°/18 mmHg	1.4437	204.8	201.9
Butyl monochloroactate	178–180°	1.4271	745.4	749.8
2-Ethylhexyl monochloroacetate	123–124°/16 mmHg	1.4395	542.9	545.1
Lauryl monochloroacetate	158–160°/5 mmHg	1.4468	443.9	445.0

8) C. F. H. Allen and J. Van Allan, *Org. Synth.*, **24**, 82.

9) W. S. Johnson and W. P. Schneider, *Org. Synth.*, **30**, 20.

Syhntheses of 2, 3-epoxy-3-methyladipic esters. Synthesis of the di-*n*-butyl esters (*a*) *Use of sodium amide as condensing agent.*—To a mixture of 86 g. (0.5 mol.) of *n*-butyl levulinate, 75 g. (0.5 mol.) of *n*-butyl monochloroacetate and 100 ml. of dry benzene in a 500-ml. three-necked round-bottomed flask was added 25 g. (0.6 mol.) of pulverized sodium amide over a period of 2 hrs. with mechanical stirring. The temperature was kept at 15–20°C in a water bath. After addition had been completed, the mixture was stirred for 2 hrs. more at room temperature. The mixture was poured upon 350 g. of cracked ice with hand stirring. The organic layer was separated and the aqueous layer was extracted with 100 ml. of benzene. The combined benzene solution was washed with three 100-ml. portions of water, dried with anhydrous sodium sulfate, and benzene was removed under diminished pressure. The product (90 g.) was distilled in vacuo to give 25 g. of the desired ester, b. p. 148–149°C/1.5 mm Hg, n_D^{20} 1.4478, d_4^{20}1.023, S. V. 395.9 (calcd.for the dibutyl ester 391.8).

Found: C 62.80%; H 9.20%. Calcd. for $C_{15}H_{27}O_5$: C 62.91%; H9.15%.

Other experiments were conducted in exactly the same way as the above, but the temperature was kept at 5°C. Only a few grams of the di-*n*-butyl ester were obtained.

(*b*) *Use of potassium tert-butoxide as condensing agent.*—A mixture of 25.5 g. (0.15 mol.) of *n*-butyl levulinate, 22.5 g. (0.15 mol.) of *n*-butyl monochloroacetate was placed in a 500-ml. four-necked round-bottomed flask, fitted with a stirrer, thermometer and dropping funnel containing *tert.*-butyl alcohol solution of potassium *tert.*-butoxide (from 5.88 g. of the metal). The reaction was carried out with mechanical stirring in an atmosphere of dry nitrogen. The alcoholate was added during one hour, and then the mixture was stirred for one hour. The temperature was kept at 25–30°C. From the reaction mixture *tert.*-butyl alcohol was removed as much as possible under diminished pressure on a steam bath. After addition of water the product was extracted successively with three 100-ml. portions of ether. The combined ether solution was washed with 50 ml. of water and dried with anhydrous sodium sulfate. The product (35.8 g.) was distilled in vacuo to give 20.5 g. (48% yield) of colorless fraction, b.p. 189–191°C/15 mm Hg, n_D^{20} 1.4458, d_4^{20} 1.021, S. V. 389.1 (calcd. for the dibutyl ester 391.8).

Found: C 62.56%; H 9.25%. Calcd. for $C_{15}H_{27}O_5$: C 62.91%; 9.15%.

Other experiments were conducted in exactly the same way as the above, but the temperature was kept at 5–10°C, and 30–38% yields were procured.

(*c*) *Attempted use of sodium ethoxide as condensing agent.*—To a mixture of 86 g. (0.5 mol.) of *n*-butyl levulinate and 75 g. (0.5 mol.) of *n*-monochloroacetate, cooled in an ice-salt bath, 40 g. (about 0.5 mol.) of freshly prepared sodium ethoxide was added over a period of 4 hrs. The mixture was then stirred for 9 hrs. with cooling, 2 hrs. at room temperature, and finally 6 hrs. with warming on a water bath, and then poured on ice water. The mixture was acidified with acetic acid, and the product was extracted with ether. The ether layer was dried with anhydrous sodium sulfate, and the ether was removed under diminished pressure. The product (60 g.) was distilled in vacuo, b.p 150°C/2.5 mm Hg, n_D^{20} 1.4688, S. V. 554.1 (calcd. for the dibutyl ester 391.8).

(*d*) *Attempted use of sodium methoxide as condensing agent.*—The synthesis was conducted similarly to the above. To a mixture of *n*-butyl monochloroacetate (0.5 mol.), *n*-butyl levulinate (0.5 mol.) and 200 ml. of dry benzene was added 54 g. (0.8 mol.) of sodium methoxide. The product (60 g.) was distilled in vacuo to give 24 g. of yellow fraction, b.p. 128–130°C/3 mmHg, n_D^{20} 1.4701, S. V. 584.6 (calcd. for the dibutyl ester 391.8).

Syntheses of the 2-ethylhexyl-(1)-*n*-butyl-(6), *n*-Butyl-(1)-2-ethylhexyl-(6), Di-2-ethylhexyl, Lauryl-(1)-*n*-butyl-(6), *n*-Butyl-(1)-lauryl-(6), Lauryl-(1)-2-ethylhexyl-(6), and 2-Ethylhexyl-(1)-lauryl-(6) esters.—These seven 2, 3-epoxy-3-methyladipates were synthesized from 0.5 mol. of the monochloroacetate and 0.5 mol. of the levulinate by 0.6 mol. of sodium amide in a way exactly similar to the method of synthesis of the di-*n*-butyl ester using sodium amide, and are represented in Table I.

Synthesis of the Di-lauryl ester (*a*) *Use of sodium amide as condensing agent.*—A mixture of 137 g. (0.5 mol.) of lauryl levulinate, 126 g. (0.5 mol.)of lauryl monochloroacetate and 100 ml. of dry benzene was used with 25 g. (0.6 mol.) of sodium amide. The properties of the ester are recorded in Table I.

(*b*) *Use of potassium tert-butoxide as condensing agent.*—To a mixture of 41.0 g. (0.15 mol.) of lauryl levulinate and 37.8 g. (0.15 mol.) of lauryl monochloroacetate was added potassium *tert.*-butoxide prepared from 5.88 g. (0.15 mol.) of potassium. The method of synthesis was exactly similar to that of the di-*n*-butylester. As a residue of the first vacuum distillation (over 150°C/ i2 mm Hg), the crude desired ester was obtained n 34% yield, S. V. 221.5 (calcd. for the dilauryl ester 219.7).

Summary

Levulinic and monochloroacetic esters are condensed by sodium amide or potassium *tert.*-butoxide to give the corresponding 2, 3-epoxy-3-methyladipic esters. *n*-Butyl (B), 2-ethylhexyl (O), and lauryl (L) alcohols were used as alcoholic components of these starting esters. Although the yields were poor, nine new esters, namely the B-B, B-O, O-B, B-L, L-B, O-O, O-L, L-O,and L-L 2, 3-epoxy-3-methyladipates were obtained.

As for condensing agents, potassium *tert.*-

butoxide was the most excellent, and sodium amide gave also good results, while sodium ethoxide and methoxide gave no desired ester.

These new esters would be able to be utilized as a stabilizing plasticizer for polyvinyl chloride.

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Molecular Structures of Propylene Oxide and Epichlorohydrin by Electron Diffraction

By Masato IGARASHI

(Received August 6, 1954)

In the previous report[1], it was stated that the molecular structure of ethylene oxide was reinvestigated by electron diffraction and the results coincided better with those of the microwave investigation[2] than those of the early electron diffraction study[3].

In the present paper electron diffraction studies about the structures of propylene oxide and epichlorohydrin are reported.

Propylene oxide and epichlorohydrin have a ring of ethylene oxide and the chief aim of these studies is to know the configuration of $-CH_3$ in propylene oxide and $-CH_2Cl$ in epichlorohydrin with respect to the ring.

Procedure

Propylene oxide was prepared from lime and propylenechlorohydrin which had been obtained from propyleneglycol and hydrogen chloride gas (b. p. 35–36°C). Epichlorohydrin was purified by distillation of the commercial product (b. p. 115°C).

Electron diffraction photographs were prepared by the apparatus described in the previous report[1]; the camera distance at that time was about 9 and 10 cm., and the wave length of the electron beam was about 0.055 Å. Visual intensity curves V_1 (propylene oxide) and V_2 (epichlorohydrin) were drawn from measurements of the photographs (Figs. 1 and 2). The q values of maxima and minima are shown in Tables III and IV.

TABLE I

STRUCTURE OF ETHYLENE OXIDE BY MICROWAVE INVESTIGATION[2]

C–C	1.472Å	C–O	1.436Å
C–H	1.082Å		
∠H–C–H	116°41′	∠H_2–C–C	159°25′

1) M. Igarashi, This Bulletin, **26**, 330 (1953).
2) G.L. Cunningham, A.W. Boyd, R.J. Myer, W.D. Gwinn and W.I. Le Van, *J. Chem. Phys.*, **19**, 676 (1951).
3) P.C. Ackermann and J.E. Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

TABLE II

MODELS FOR PROPYLENE OXIDE (A, B, C, D) AND EPICHLOROHYDRIN (E, F, G, H, I, J, K)

Model	C_2-C_3 Å	Angle between C_2-C_3 and C_1C_2O plane	Configuration of Cl atom in epichlorohydrin
A	1.54	58°	
B	1.50	58°	
C	1.54	50°	
D	1.54	65°	
E	1.54	58°	*trans* against the midpoint of C_1-O
F	1.50	58°	
G	1.54	50°	
H	1.54	65°	
I	1.54	58°	*cis* against the midpoint of C_1-O
J	1.54	58°	*trans* against C_1
K	1.54	58°	*trans* against O

Triangle C_1C_2O, C_1-H and C_2-H are equal to those of ethylene oxide (Table I). C_3-H= 1.09Å, C_3-Cl=1.76Å. Angles in $-CH_3$ and $-CH_2Cl$ are all equal to tetrahedral angle.

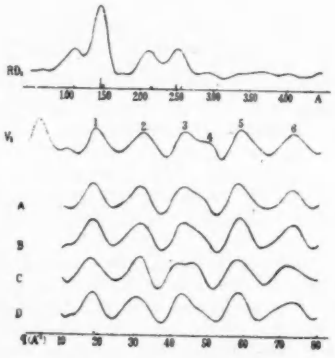


Fig. 1. Propylene oxide.

TABLE III

PROPYLENE OXIDE

Max.	Min.	q_{obs}	q_{calc}/q_{obs} A	B	C	D
1		18.3	0.983	0.988	0.972	1.004
	2	25.05	0.943	0.947	1.003	0.947
2		31.45	0.982	0.992	0.982	0.970
	3	37.25	0.988	1.001	0.974	1.001
3		42.1	1.014	1.016	0.998	1.012
	4	45.85	(0.992)	(1.012)	(0.949)	(1.025)
4		49.4	(0.042)	(1.042)	(0.929)	(0.982)
	5	52.4	0.992	0.998	0.982	1.001
5		57.8	1.000	1.007	1.000	1.000
	6	65.4	1.025	0.987	1.006	0.983
6		72.2	1.004	1.007	0.991	1.015
	7	78.75	0.992	0.977	1.013	1.001
7		(84.0)				
Average, 10 features			0.994	0.994	0.991	0.994
Average deviation			0.015	0.012	0.012	0.017

TABLE IV

EPICHLOROHYDRIN

Max.	Min.	q_{obs}	q_{calc}/q_{obs} E	F	G	H
1		11.9	(0.908)	(0.950)	(0.908)	(0.915)
	2	14.45	(0 920)	(0.920)	(0.906)	(0.934)
2		17.1	0.977	0.954	0.971	0.983
	3	20.05	1.006	(1.021)	1.001	1.011
3		21.3	0.994	(1.008)	1.008	1.008
	4	23.25	1.002	1.006	0.998	1.024
4		26.25	**1.002**	**1.006**	**0.998**	**1.014**
	5	29.05	0.992	0.999	0.978	1.024
5		31.9	**0.991**	**0.998**	**0.982**	**0.994**
	6	34.7	0.994	1.008	0.988	1.000
6		37.05	1.007	1.001	1.001	1.001
	7	39.35	0.973	0.986	0.970	1.001
7		41.6	0.993	1.003	0.979	1.017
	8	44.0	0.991	0.998	0.984	1.000
8		46.95	**0.991**	**1.003**	**0.986**	**0.995**
	9	49.65	0.984	(1.016)	0.982	1.013
9		51.05	1.005	(1.019)	0.999	1.027
	10	53.2	1.004	(1.006)	0.996	1.021
10		56.8	**1.011**	**1.014**	**0.998**	**1.026**
	11	58.95	0.997	1.011	0.984	(1.017)
11		60.8	**0.995**	**0.998**	**0.998**	**1.003**
	12	64.7	0.998	1.003	0.998	1.003
12		70.0	1.023	1.024	1.011	....
	13	77.25	1.019	1.022	1.020	....
13		(82.25)				
Average			0.998	1.002	0.992	1.008
Average deviation			0.009	0.009	0.010	0.010

Values in Gothics were doubly weighted in computing averages.

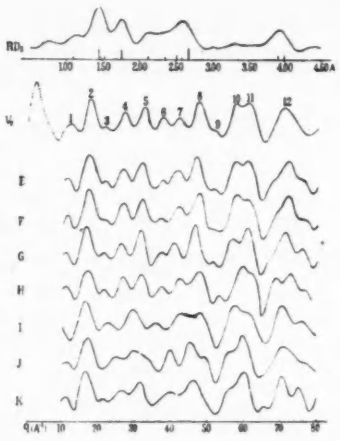
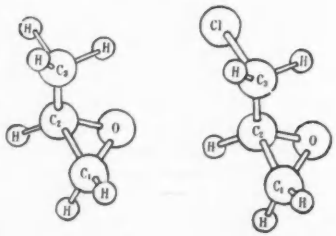


Fig. 2. Epichlorohydrin



Propylene oxide Epichlorohydrin

Fig. 3. Perspective picture of propylene oxide and epichlorohydrin molecules.

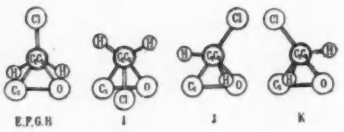


Fig. 4. Various configurations of epichlorohydrin.
H-atoms of C_1H and C_2H are omitted for convenience.

Analysis and Results

From the visual intensity curves V_1 and V_2, radial distribution curves RD_1 (propylene oxide) and RD_2 (epichlorohydrin) were drawn by using the formula,

$$rD(r)=\sum_{q=1,2,\cdots}^{q=80} V(q)\exp(-aq^2)\sin(\pi qr/10)$$

where $q=10s/\pi=(40/\lambda)\sin\phi/2$, ϕ the scattering angle, and a was determined such that $\exp(-aq^2)=0.1$ at $q=80$.

In RD_1 main peaks are at 1.10, 1.44, 2.11, 2.51 and 2.92 Å, which seem to correspond to the distances C−H, (C_1-C_2, C−O, C_2-C_3), ($C_1\cdots H$, $O\cdots H$), ($C_1\cdots C_3$, $C_3\cdots O$) and long range ($C\cdots H$, $O\cdots H$), respectively.

In RD_2 main peaks are at 1.14, 1.45, 1.76, 2.13, 2.60 and 3.93 Å, which seem to correspond to the distances C−H, (C_1-C_2, C−O, C_2-C_3), C_3−Cl, ($C\cdots H$, $O\cdots H$), ($C_1\cdots C_3$, $C_3\cdots O$, $C_2\cdots Cl$) and ($C_1\cdots Cl$, $O\cdots Cl$), respectively.

Making reference to the radial distribution curves and the results of ethylene oxide, molecular models for the correlation method were constructed in the ranges as follows, C_1-C_2; 1.44–1.56 Å, $C_1-O=C_2-O$; 1.43–1.45 Å, C_2-C_3; 1.50–1.58 Å, angle between C_2-C_3 and C_1C_2O plane; 50°–70°.

Among them models A, B, C, D (propylene oxide) and E, F, G, H, I, J, K (epichlorohydrin) are described here (Table II and Figs. 3 and 4).

In models E, F, G and H, Cl atom is *trans* against the midpoint of C_1–O. Models I, J, K for epichlorohydrin in which Cl atom is in different configuration from those of E, F, G and H, are also used for comparison.

Theoretical intensity curves for these models were calculated from the equation,

$$I(q)=\sum_{i,j}(Z_iZ_j/r_{ij})\exp(-b_{ij}q^2)\sin(\pi qr_{ij}/10)$$

where r_{ij} is the distance between atoms i and j, and Z_i is the atomic number of atom i, apart from the value 1.25 for the hydrogen atom. The coefficient b_{ij} was assumed to be 0.00016 for bonded hydrogen terms, 0.0004 for unbonded hydrogen terms, and zero for all the others.

Propylene Oxide.—From the correlation between visual and theoretical intensity curves and the values q_{calc}/q_{obs} (Table III), model B seems to be the best among them.

The main results are as follows; $C_2-C_3=1.52\pm0.03$ Å, the angle between C_2-C_3 and C_1C_2O plane is equal to 58°±5°. This angle is almost equal to that between C−H and C_1C_2O plane of ethylene oxide studied by microwave spectrum[2].

Epichlorohydrin. — Theoretical intensity curves of models E, F, G and H which are *trans* in reference to Cl atom and the midpoint of C_1-O, are in good accordance with the visual intensity curve, though the max. 6 is a little weaker than visual. Among them E and F are better than the others according to the value q_{calc}/q_{obs} (Table IV). As the curves of H, I and J are very different from the visual, these configurations would scarcely be worthy of further consideration.

The main results are as follows; $C_2-C_3=1.52\pm0.03$ Å, the angle between C_2-C_3 and C_1C_2O plane is equal to 58°±5°. They are

equal to those of propylene oxide. The configuration of Cl atom is almost *trans* against the midpoint of C_1-O.

The author wishes to express his gratitude to the late Professor H. Oosaka and Professor A. Kotera for their kind guidance during the course of this research. He also owes much to Mr. M. Yamaha to whom his thanks are due.

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The Role of Ethylene Glycol and Polyethylene Glycol in the Freeze-Thaw Stability of Synthetic Latex

By Seizo OKAMURA and Takuhiko MOTOYAMA

(Received August 9, 1954)

Introduction

One of the most important properties of synthetic latex is its freeze-thaw stability, and it is necessary to study this property for industrial application. In the paint industry it is usual to employ the freeze-thaw test in order to determine the stability. Recently Digioia and Nelson[1] have reported freeze-thaw cycles of certain commercial synthetic latices. However, they have not mentioned either the sources or the conditions of the freezing stability. The freeze-thaw test is widely used for the checking of the commerciability of the emulsion, but there is lack of reliable data in quantitative studies concerning it. In the present work the adsorption of ethyleneglycol and of polyethyleneglycol by the emulsion particles of various polyvinyl compounds was studied with reference to the conditions under which freeze stability was attainable.

Experimental

The monomers used are styrene (St.), methylmethacrylate (MMA.), methylacrylate (MA.), vinylacetate (VAc.) and acrylonitrile (AN.). These are purified by vacuum distillation. The polymerization catalyst used is ammonium persulfate, commercial c.p. grade; and the emulsifier mainly employed is sodium-dodecylsulfate, recrystallized twice in ethanol solution. The emulsion polymerization of MMA., MA., VAc. and AN. is carried out at 60°C in still-stand, and that of St. at 80°C in agitation, both for 5 hrs. The concentration of catalyst is 0.1%, and the ratio of monomer to aqueous solution is 0.08.

The freezing process of the emulsion obtained is accomplished by cooling it at -17.5 ± 2.5°C for 24 hrs. If the latex prepared by the addition of glycols is stable enough after its thawing at room temperature, its second freezing is conducted at the same temperature for as many hours, and further its third, if stable, like the second, for 45 hrs. In almost all these cases stability is observed in the second and the third process of the test only when the first process of the test has been satisfactory.

Results and Discussion

1. Preliminary Experiments on the Addition of Ethyleneglycol.—The experiments are shown in Table I. In this table X-marks represent the unstable cases and 0-marks the stable.

TABLE I

EXAMPLES OF THE LATICES OF PVAc. AND PMMA.

Kind of Monomer	Kind (& Amount) of Emulsifier used in Polymerisation	Kind (& Amount) of Stabilizer	Freezing 1st.	2nd.	3rd.
VAc.	None	None	x		
〃	N. (0.5%)	〃	x		
〃	A. (〃)	〃	x		
〃	K. (1.0%)	〃	x		
〃	PVA. (0.5%)	〃	x	Slightly	
〃	None	Ethyleneglycol (5%)	0	x	
〃	〃	〃 (10%)	0	0	0
〃	N. (0.5%)	〃 (3%)	0	0	0
MMA.	A. (0.1%)	〃 (3%)	x		
〃	〃 (0.2%)	〃 (〃)	0	0	0
〃	〃 (0.5%)	〃 (〃)	0	0	0
〃	〃 (0.5%)	None	x		
〃	K. (1.0%)	Ethyleneglycol (10%)	x		

N. Polyethyleneoxide-dodecylether having $\bar{P}$=45
A. Sodium dodecylsulfate
K. Cetyltrimethylammoniumbromide
PVA. Polyvinylalcohol having $\bar{P}$=ca. 1000

1) F.A. Digioia and R.E. Nelson, *Ind. Eng. Chem.*, 45, 745 (1953).

2. The Minimum Amount of Ethyleneglycol Required for Stabilization.—The freeze-thaw stability can be measured by the determination of the minimum amount of glycol required for the stabilization of the latex. The curves indicating the concentrations of ethyleneglycol versus that of emulsifier are given in Figure 1.

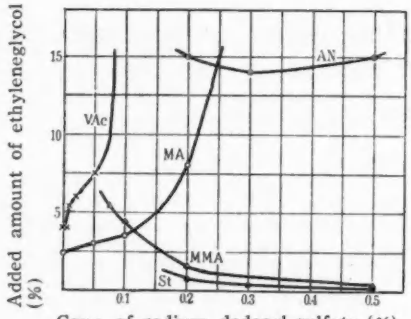

Fig. 1. The minimum amount of glycol required in various types of emulsions polymerized with sodium-dodecylsulfate.

As shown in Fig. 1, these curves are classified into three groups, the first is the case of St. and MMA., the second MA. and VAc., and the third AN. The amount of glycol required decreases in the first groups and increases in the second, and finally is constant in the third, as the concentration of emulsifier increases. In the range of this work, the monomers of the first group are more hydrophobic and those of the second more hydrophilic. An. is most hydrophilic in the monomer state but relatively hydrophobic in the polymer. It may, therefore, be concluded that the facility of stabilization attained by the addition of glycol increases as the hydrophobic property of the monomers or the polymers increases.

From Figure 2 it will be noticed that the amount of glycol required for stabilization is small in the case of using relatively high molecular weight compds, such as polyethyleneglycol as emulsifiers. As shown in the comparison of Fig. 1 and Fig. 2, the freeze-thaw stability is attained more easily in the nonionic than in the anionic detergents. Also in Fig. 2 the order of hydrophobic nature, (St.>MA.>VAc.) is shown as parallel to the order of properties for stabilization.

In all the five monomers the latices obtained with cetyltrimethylammoniumbromide (concentration range 0.7–2.0%) could not be stabilized by the addition of ethyleneglycol (to 20%).

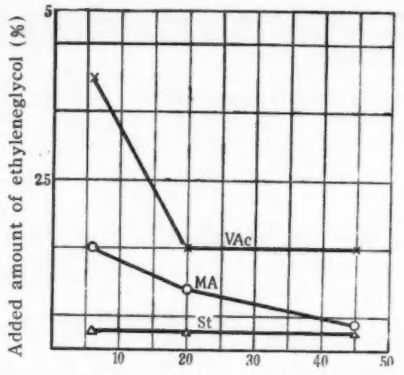

Fig. 2. The minimum amount of glycol required in three types of emulsions polymerized with polyethyleneoxidedodecylether having various degrees of polymerization.

3. The Properties of Stabilized Latices for Freeze-thaw A) Depression of the Freezing Point of Latices.—The value of the freezing point of emulsion must be equal to that of its aqueous solution because the size of its molecules is much larger than of those of the dispersing medium. The depression measurement indicates therefore the decrease of the concentration of glycol in the aqueous solution. Table II represents the comparison of the value of freezing point depression in the aqueous solution of ethyleneglycol and that in the stabilized latices.

TABLE II
THE FREEZING DEPRESSION OF STABILIZED LATICES

Concentration of glycol (g./l.)	15	45	75
Depression in aqueous solution (°C)	0.46	1.46	2.54
Depression in stabilized AN.-latices (°C)	0.46	1.40	2.33
Depression in stabilized St.-latices (°C)	0.36	1.22	2.12

Table II shows that the St.-latex which is most easily stabilized has the lowest depression value and that the adsorption of glycol on emulsion particles has occurred in the St.-latices.

B) The Electrophoretic Mobility of Stabilized Latices.—The electrophoretic mobility of emulsion has been determined by the present researchers. As previously reported, it has been shown to alter by the adsorption of detergents. It is also suggested that the electrophoretic mobility changes by the adsorption of different solvents having different

dielectric constants[2]. The partition of additives between the solution and the particles may be sensitive to the mobility. Thus the changes of mobility by stabilization are measured by the usual U-type assembly previously reported[3]. The results of the experiment are plotted in Figures 3 and 4.

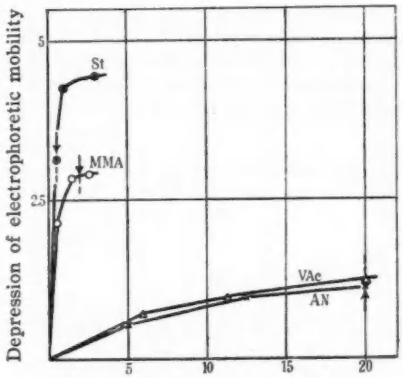

Fig. 3. The decrease of the electrophoretic mobility after the addition of ethyleneglycol (Emulsifier used was sodium dodecylsulfate 0.2%.).

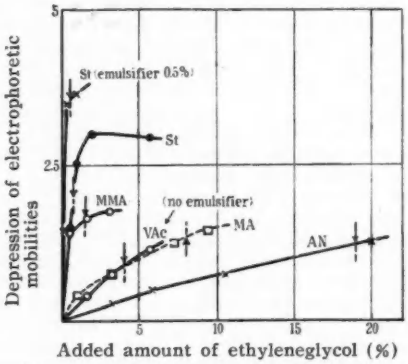

Fig. 4. The decrease of the electrophoretic mobility after the addition of polyethyleneglycol 300 (U.C.C. Ltd.) (Emulsifier used was sodium dodecylsulfate 0.2%).

As shown in Figs. 3 and 4, the order of the change of mobility is in good agreement with the order of the facility of stabilization. The stabilized points in each latex are marked with arrows which are in the neighbourhood of the saturation. The ratios of the mobilities of the stabilized latices to those of the originals are tabulated in Table III.

It is of interest to note that the average value of these ratios agrees with the ratio of dielectric constants of ethylene glycol and that of water, 41.2 (d.c. of glycol)/81.0 (d.c. of water)=0.508.

C) The Adsorption of Additives on Emulsion Particles.—It is necessary to determine directly the amount of adsorption of additives for the investigation of freeze-thaw stability. Fortunately the concentration of ethyleneglycol and polyethyleneglycol in aqueous medium can be measured quantitatively by the periodic acid (volumetric) method[5], and by the Shaffer (gravimetric) method[4] respectively. Figure 5 gives the case of ethyleneglycol and Figure 6 that of polyethyleneglycol.

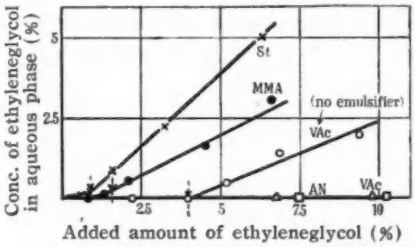

Fig. 5. The adsorption of ethyleneglycol on the emulsion particles (Arrows show points which have attained stability.). (emulsifier: Sodium dodecylsulfate 0.2%)

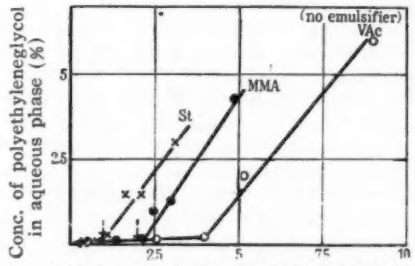

Fig. 6. The adsorption of polyethyleneglycol on the emulsion particles (Arrows show points which have attained stability.). (emulsifier: Sodium dodecylsulfate 0.2%)

TABLE III

RATIOS OF THE MOBILITIES OF THE STABILIZED AND UNSTABILIZED LATICES

Kind of Emulsion	St.	St.	MMA.	MA.	VAc.	AN	Average
Kind of Emulsifier	A	A	A	A	None	A	—
Conc. of Emulsifier	0.5	0.2	0.2	0.2	—	0.2	—
Ratio of Mobilities	0.49	0.67	0.58	0.57	0.59	0.48	0.56

2) E.K. Rideal, "An Introduction to Surface Chemistry," Camb., p. 406.

3) T. Motoyama and S. Okamura, *Mem. Fac. Eng. Kyoto Univ.*, 15, 242 (1653).

4) C.B. Shaffer and F.H. Critchfield, *Ind. Eng. Chem.*, 19, 32 (1947).

5) G.O. Curme and F. Johnston, "Glycols," Reinhold, (1952).

As represented in Figs. 5 and 6, the points of saturated adsorption coincide with the stabilizing points (shown as arrows in figures). Also the Figures indicate that the facility of saturated adsorption agrees with that of stabilization, (St.>MMA.>VAc.>AN.)

Summary

The freeze-thaw stability of synthetic latices obtained by the emulsion polymerisation of styrene, methyl methacrylate, methyl acrylate, vinyl acetate and acrylonitrile has been measured at the freeze-thaw cycles of −17.5°C and room temperature. It is found that the addition of ethyleneglycol and polyethyleneglycol into the latices increases the stability. The freezing point depression and the electrophoretic mobility of stabilized latices indicate the adsorption of stabilizing additives on the emulsion particles. Finally the adsorption of ethylene glycol and polyethylene glycol on the emulsion particles is determined directly. In consideration of these experimental results the freeze-thaw stability seems to be attained by the adsorption of additives on the emulsion particles.

The authors are grateful to Professor Ichiro Sakurada for his interest in this work.

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Surface Chemistry of High Polymers. VI. The Monolayer of Polyethylene Terephthalate and Poly-N-vinyl Pyrrolidone

By Hiroshi HOTTA

(Received August 10, 1954)

Although we studied the monolayer of various linear polymers up to the preceding paper, these polymers consist of chains alone either in the main chain or in the side chain.[1-5] In order to obtain some information in respect to the contribution of the ring group in the side chain as well as in the main chain to the behavior of surface film, we studied the monolayer of polyethylene terephthalate and poly-N-vinyl pyrrolidone by the measurements of interfacial pressure and potential at the air/water and oil/water interfaces. It was found as the results of the present investigation that the ring groups in the main chain make the polymer molecule rigid even at the oil/water interface, while that in the side chain is not essentially different from the chain groups. Further more the study of the hydrolysis of poly-N-vinyl pyrrolidone by the monolayer technique provides a useful inference concerning it.

Experimental

Polyethylene terephthalate was spread from the solution of the mixture of benzene and cresol (1: 1) at the air/water and benzene/water interfaces using a micrometer syringe. The distilled water was used as the water phase.

Poly-N-vinyl pyrrolidone, whose molecular weight is 13,400, was spread from the aqueous solution containing 20% pyridine at the air/water and petroleum ether/water interfaces. The pH of the substrate was adjusted with hydrochloric acid or sodium hydroxide as in the previous papers[4,5] to investigate the effect of hydrolysis.

Both materials were kindly supplied from Prof. S. Murahashi of our Institute.

The interfacial pressures at the air/water and oil/water interfaces were measured by the hanging plate method[1] and ring method[2], respectively, as in the previous papers. The interfacial potential at both interfaces was measured by the vibrating electrode method.[1,5] The detailed descriptions of spreading technique and of measurements were already given in the previous papers. The only different technique adopted in the present investigation is that the area at the air/water interface was changed by the successive injection method for poly-N-vinyl pyrrolidone, which was already reported in the first paper.[1] The surface moment-area curve, shown by dotted lines and denoted with prime in Figs. 1 and 4, was calculated from observed surface potential using the Helmholtz's formula as usual.[1]

Results and Discussion

A. Polyethylene Terephthalate.—The surface potential and moment at the air/water interface (15°C) plotted against area per residue are shown in Fig. 1. The reliable value of surface potential was obtained at a smaller area than 115 Å² per residue, and became

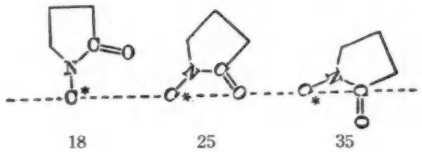
1) T. Isemura, H. Hotta and T. Miwa, This Bulletin, 26, 380 (1953).
2) H. Hotta, ibid., 26, 386 (1953).
3) H. Hotta, ibid., 27, 80 (1954).
4) T. Isemura, H. Hotta and S. Otsuka, ibid., 27, 93 (1954).
5) H. Hotta, ibid. 27, 412 (1954).

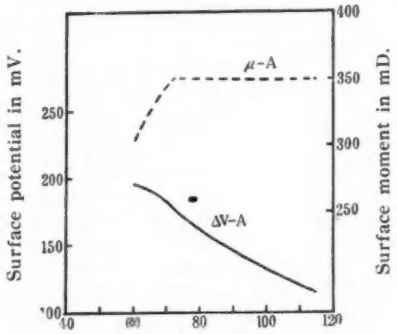
constant at 62 Å² per residue. The corresponding surface moment was kept constant to 350 mD. up to about 72 Å² per residue Therefore, the surface moment of 175 mD. might be attributed to a single group of

in this constant range. When we consider the magnitude and direction of each polar bond in this group,[6] the model proposed in Fig. 2 is entirely consistent with Table I in the third paper[3] showing the relationship between the value of surface moment and the inclination of C=O bond at the surface. Thus, this table would be useful for estimating the inclination of C=O bond at the surface for an unknown polymer.

TABLE I

THE STATE OF POLY-N-VINYL PYRROLIDONE AT THE OIL/WATER INTERFACE

Model			
Oil / Water			
Most compact area estimated from Fig. 4 in Å² per residue	18	25	35
Surface moment in mD.	210	290	350



Area in Å² per residue

Fig. 1. The surface potential (ΔV) (or moment (μ))-area curve of polyethylene terephthalate at the air/water interface.

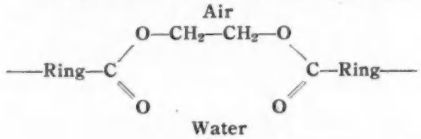
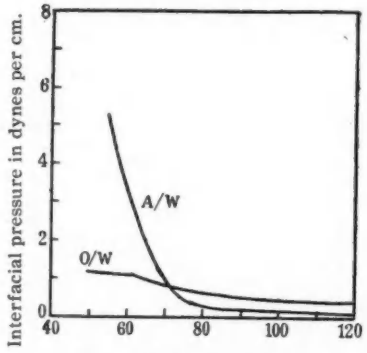


Fig 2

Although the surface pressure at the air/water interface was measured by the hanging plate method using a glass barrier for compression, the film was so gelatinous that a hanging plate, which was once raised with compression, did not return to an equilibrium position during moderate experimental time. Especially, it was recognized that the plate was considerably displaced horizontally as the area of the film was decreased to less than about 72 Å² per residue, from which the surface moment begins to decrease. Therefore, since the true surface pressure could not be obtained, a tentative curve for it is shown in Fig. 3 (15°C).



Area in Å² per residue

Fig. 3. The interfacial pressure of polyethylene terephthalate at the air/water (A/W) and benzene/water (O/W) interfaces.

Although the attempt was made at first the interfacial pressure to measure at the petroleum ether/water interface, we failed to measure it due to the slow desorption of cresol in the spreading solution from the surface. Then, it was measured at the benzene/water interface (15°C) as shown in Fig. 3. The kink point of this curve (62 Å² per residue) corresponds to the area where the surface potential at the air/water interface attained a constant value. This area may be very plausible as the area occupied by the model proposed in Fig. 2. By using the extrapolated value of the product of interfacial pressure and area to infinite area as

6) C.P. Smyth, *J. Am. Chem. Soc.*, 60, 183 (1938).

already reported,[2,3] the degree of polymerization for the segment as a statistical kinetic unit at the oil/water interface is estimated to be 13. Although the detailed interpretation for this value will be given elsewhere with other polymers,[7] it is concluded that the ring groups in the main chain make the polymer molecule rigid and should be interpreted in the light of a different base from the chain groups.

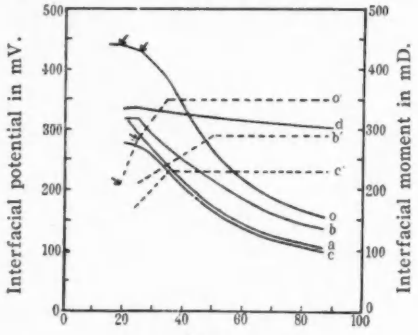


Fig. 4. The interfacial potential (—) (or moment (...))-area curve of poly-N-vinyl pyrrolidone (curve a, pH 0.3, 0.8, curve b, pH 1.4, 3.8, 4.5, and curve c, pH 5.6–11.4) by successive injection method, (curve d, pH 3.8, 5.6) by compression of glass barrier at the air/water interface, and (curve o, pH 0.4–9.0) at the petroleum ether/water interface.

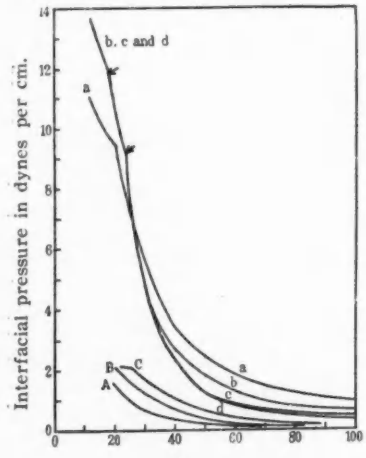


Fig. 5. The interfacial pressure of poly-N-vinyl pyrrolidone at the air/water interface (curve A, pH<0.8, curve B, pH 1.4–7.4 and curve C, pH 11.0) and at the petroleum ether/water interface (curve a, pH 0, curve b, pH 0.4, 1.4, 3.6, 4.6, curve c, pH 5.7, 7.5, 11.0, and curve d, pH 11.6).

7) H. Hotta, *J. Colloid Sci.* **9**, 504 (1954).

B. Poly-N-vinyl Pyrrolidone.—When the film was compressed, for the measurement at the air/water interface, by using a glass barrier as usual, the obtained surface potential was very abnormal as shown as curve d in Fig. 4. It is presumably because the molecules are not spread or compressed uniformly all over the surface. Therefore, the successive injection method using a micrometer syringe was adopted instead of compression by barrier, for, in this case, the film is spread in a small place so as to avoid to some extent the lack of uniformity as mentioned above. The obtained results of surface potential (or moment) and pressure (19±1°C) were grouped as shown in Figs. 4 and 5, respectively.

The interfacial potential (or moment) (20±1°C) and pressure (8±1°C) at the petroleum ether/water interface were also shown in Figs. 4 and 5, respectively. The interfacial potential at the pH between 0.4 and 9.0 lay on a single curve o in Fig. 4. Those at pH 10.0 and 11.0 were somewhat lower than that shown by this curve at the larger area than about 70 Å² per residue. That on pH 11.8 was furthermore lower at the larger area than about 50 Å² per residue, but identical at the smaller area. However, we had to wait for a long time to obtain the equilibrium value at the higher pH than 9. This fact and the trend of some fluctuation for observed value show that there may be some lack of uniformity even at the oil/water interface. The values of the product of interfacial pressure and area per residue extrapolated to infinite area are shown in Fig. 6 as the function of the pH of substrate.

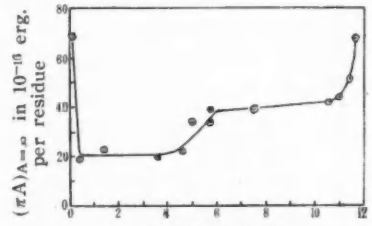


Fig. 6. The product of interfacial pressure (π) and area per residue (A) of poly-N-vinyl pyrrolidone extrapolated to infinite area plotted against the pH of substrate.

From these facts, it is concluded that the behavior of this film is different according to the acidity or alkalinity of the substrate, and affected more sensitively by alkali than acid. However, the evidence of this difference is somewhat obscured by the non-uniformity of compression as mentioned above.

This non-uniformity is so considerable in the pH range to show the effect of the substrate that we could not confirm the extent of change with the pH sufficiently accurately. On the other hand, Frank had found on studying the lactam-amino acid equilibrium at 100°C that this polymer is more labile in the alkaline solution in contrast with the acidified solution[8]. His result is also qualitatively consistent to the present result.

The trend shown in Fig. 6 gives another evidence of the above conclusion. The value on the acidified substrate is almost identical to that of polyvinyl acetate[2], which has the massive side chains lying at the interface similar to this polymer. The value on the alkaline substrate does not show any serious change of structure, but only a small change such as hydration. Such a hydration is conceivable when we consider the instability in the alkaline solution mentioned above[8]. The high value at both the extremes of pH in Fig. 6 is presumably owing to the partial hydrolysis, but its extent in the pH range shown in Fig. 6 should be very small in the light of the value of interfacial potential at these pH especially at the smaller area. Such a fact was previously reported in the case of polymethacrylic acid[4].

The interfacial moment at the oil/water interface in Fig. 4 is kept constant to 350 mD. up to 35 Å^2, decreases rapidly to 290 mD. at 25 Å^2 and furthermore to 210 mD. at 18 Å^2 per residue, namely, at the collapse point. The latter two kink points shown by arrows in Fig 4 appear also in the interfacial pressure curve at the same areas as shown by arrows in Fig. 5, respectively. Therefore, the film is considered to be transformed at these areas with the fair change of hydrophility of polar groups. Furthermore, since the bond moment of C−N bond as well as C−O bond in vacuo is small compared with C=O bond[6], the inclination of C=O bond for each state of this polymer at the oil/water interface can be estimated from Table I of the third paper[3]. The models proposed in Table I in the present paper are considered to be consistent with the previous table[3] and also with the corresponding area shown in this table taking into account the behaviour of other polymers previously investigated[1-5]. In this table carbon atom of main chain is represented by C*.

Although the surface moment at the air/water interface is somewhat uncertain due to the non-uniformity as mentioned above, the valus of curves b′ and c′ in the constant moment range at the larger area in Fig. 4 are almost identical with those at the areas of the first and second kink points of curve o, respectively. Furthermore, the largest area of maximum surface potential is also identical with the area at the first kink point of curve o. It is considered from these facts that the configuration under the above respective condition corresponds to that for the same value of surface moment in Table I. That is, as mentioned above, the difference between their respective condition is not caused by the serious change of structure, but by the small change of hydration of polar groups as shown in Table I. The model of most condensed type corresponding to curve c′ is consistent with the trend of observed value already mentioned, but apparently inconsistent with the lability of the film on alkaline substrate. Such an inconsistency is not clarified at present.

Summary

As the result of the measurements of the interfacial pressure and potential of polyethylene terephthalate and poly-N-vinyl pyrrolidone at the air/water and oil/water interfaces, it is concluded that the ring groups in the main chain make the polymer molecule rigid even at the oil/water interface, while that in the side chain is not essentially different from the chain groups. The film of poly-N-vinyl pyrrolidone is relatively labile on the alkaline substrate.

In conclusion, the author expresses his hearty thanks to Prof. T. Isemura for his kind guidance throughout the present work and to Prof. S. Murahashi of our Institute who kindly supplied valuable samples to him. The cost of this research has partly defrayed from the Scientific Research Encouragement Grant from the Ministry of Education, to which the author's thanks are due.

The Institute of Scientific and Industrial Research, Osaka University, Sakai, Osaka

8) H. P. Frank, *J. Polymer Sci.*, **12**, 565 (1954).

Studies on Fused Iron Catalyst for Alcohol Synthesis by Hydrogenation of Carbon Monoxide. III. Function of Copper in the Catalyst

By Hiroshi UCHIDA, Hideo ICHINOKAWA and Kiyoshi OGAWA

(Received August 16, 1954)

Introduction

Though the fused iron catalyst had been used in the I. G. Farbenindustrie A. G.,[1] and thereafter by R. B. Anderson,[2-4] et al. for the Fischer-Tropsch- as well as Synol-synthesis, it had never been a special catalyst for the synthesis in high yield of alcohols, but the ordinary catalyst for ammonia synthesis.

In this respect, we have been conducting a series of experiments in order to shed some light upon the fused iron catalyst for alcohol synthesis. Our preceeding experiment[5,6] revealed that the fused iron catalysts could be divided into two groups. The catalysts in one group contained Al_2O_3 and K_2O as principal promoters, and those in another group had SiO_2, MgO and K_2O as such. The catalysts of the first group could sometimes be found highly active, and gave alcohol-rich products when the synthesis was conducted at low temperatures. In the facility of producing alcohol-rich products, the catalysts in the second group, however, stood behind those of the first group, even though the synthesis could be undertaken at a considerably low temperature.

A consideration of this result has led us to expect that a catalyst suitable for alcohol synthesis may be obtained if it contains other promoters together with those found in the highly active catalyst of the first group.

The present paper deals with the experiments of the expectation, and shows the effect of the addition of copper ont he behaviour of the catalyst. The effect is to make the catalyst favorable for the production in high yield of oxygenated compounds, but to cause a decrease in the activity in water-gas synthesis.

1) P.B.R. 98, 165.
2) R.B. Anderson, and J.F. Shultz et al., *J. Am. Chem. Soc.*, **72**, 3503 (1950).
3) R.B. Anderson, and B. Seligman et al., *Ind. Eng. Chem.*, **44**, 391 (1952).
4) R.B. Anderson, and J. Feldman et al., ibid., **44**, 2418 (1952).
5) H. Uchida, and N. Todo et al., *J. Chem. Soc. Japan, (Ind. Sect.)*, **56**, 487 (1953) (in Japanese).
6) H. Uchida, and K. Ogawa et al., ibid., **57**, 100 (1954).

Experimental Procedure

The contribution of promoters in the fused iron catalyst was examined both by the activity measurement and by the analysis of synthesis products obtained with the catalyst.

Surface properties of the catalyst were simultaneously studied, in order that a better knowledge of the effect and role of the promoter might be obtained.

Preparation of Catalyst and the Synthesis.—The catalyst was prepared according to the method previously reported,[7] and was subsequently crushed to granules of 1–2 mm. diameter. Figs. 1, 2, 3, and Table I illustrate the composition of the promoters. The numerals listed in the row for promoter-composition indicate the weight percentages of the promoters which might be present in the catalyst when iron could be exactly oxidized to Fe_3O_4.

The synthesis was carried out in an electrically heated 15 mm. I. D. catalyst testing reactor into which was inserted a 7 mm. O. D. thermocouple well. Before the synthesis, the catalyst (60 cc.) was reduced in a hydrogen stream under a pressure of between 20 to 40 kg. per cm² at a space velocity of between 3,000 to 5,000 per hour. The temperature was in the range of 470–500°C. The reaction was made under a pressure kept at 25 kg. per cm² and at a space velocity for the synthesis gas (H_2 : CO = 1 : 1) of 500 per hour. It was started from a temperature where the gas contraction* could be kept below 20% for the initial 2 or 3 days, and was continued with a gradually rising temperature, until a gas contraction of 50% was attained. The temperature required for maintaining this contraction in the continued operation was taken as a measure of the relative activity.

The oily products were distilled into fractions** of a temperature difference of 20°C and subsequently analysed for alcohols, esters and carbonyl compounds by the method previously reported[5]. At the same time, the contents of carbon monoxide, hydrogen, methane, and of gaseous olefins in the exit gas were determined.

Microscopic Observation.—A preparation of a catalyst was observed under a microscope, after having been thoroughly polished and subsequently

7) G. Shima and H. Uchida, *Rep. Chem. Ind. Res. Inst. Tokyo*, **45**, 369 (1950) (in Japanese).

* Defined as $(1-E/F)\times 100\%$, where E is the volume of exit gas containing CO_2 at S.T.P. and F is the volume of feed gas at S.T.P. (30l./hr.).

** The fractional distillation was continued first under the atmospheric pressure, and then under a reduced pressure of 5 mm Hg, until the final distillation temperature attained to 200°C and 190°C respectively.

etched by hydrochloric acid. Observations were made at a definite time interval on the same region of the specimen throughout the reduction. In addition, a replica stripped from the etched surface was subjected to the electron microscopic observation.

Determination of Surface Properties of the Catalyst.—The speciments having been used for the activity measurement in the ammonia synthesis at 100 kg./cm², were employed for the surface area determination by means of B E T method from the physical adsorption isotherms of CO_2 at −78°C. The surface concentration of K_2O (+CaO)* was also estimated according to the procedure by P. H. Emmett.[8] After the measurements with CO_2, the chemisorption of CO was undertaken at −78°C according to S. Brunauer[9] in order to estimate the surface concentration of iron. The pore volumes were measured by water- and mercury-displacement method[10] to calculate the average pore radius.

Experimental Results

Activity and Oxygenated Compounds.—Cat. 101 was highly active, as shown in Fig. 1. The addition of CuO to the Cat. 101, producing Cat. 301, reduced the activity markedly, but, in turn, increased the quantity of the oxygenates in the products. The detailed measurement of the activity in relation to varying amounts of CuO and K_2O, showed that the activity tended to decrease

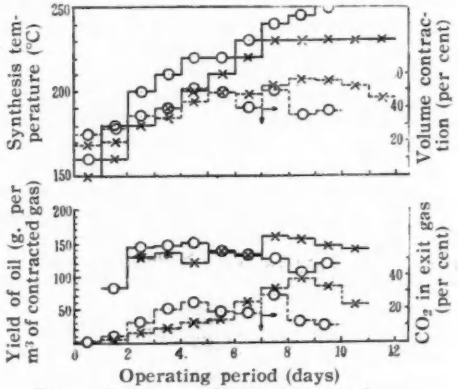

Synthesis temperature (°C)
Volume contraction (per cent)
Yield of oil (g. per m³ of contracted gas)
CO₂ in exit gas (per cent)
Operating period (days)

Fig. 1-3 Above; Temperatures of operations required to maintain constant contraction.
Below; Yields of oil products, g./m³ of contracted gas and CO_2 in exit gas.
×; Cat. 101 ($2Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $1K_2O$)
○; Cat. 301 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$)

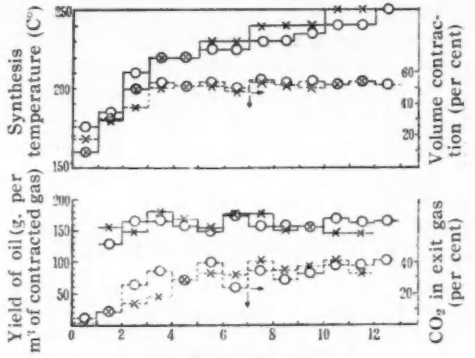

Synthesis temperature (C°)
Volume contraction (per cent)
Yield of oil (g. per m³ of contracted gas)
CO₂ in exit gas (per cent)
Operating period (days)

Fig. 2.
×; Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$)
○; Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$)

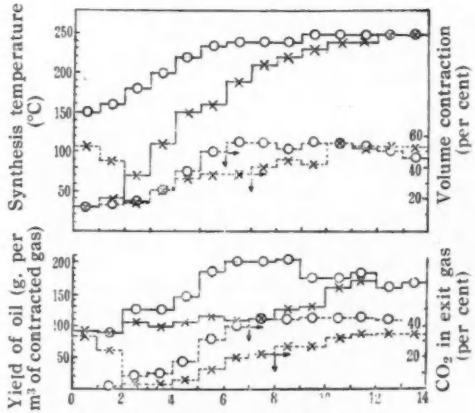

Synthesis temperature (°C)
Volume contraction (per cent)
Yield of oil (g. per m³ of contracted gas)
CO₂ in exit gas (per cent)
Operating period (days)

Fig. 3.
×; Cat. 330 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, $2.5K_2O$)
○; Cat. 331 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, 1CuO, $2K_2O$)
The ordinates below in Figs. 1-3 indicate $a \times 1000/(F-E)$; a, oil per F litres of feed gas, E, volume of exit gas containing CO_2.

with the increasing amount of CuO (0.25–0.5–1.0%) but remained unaffected by the varying amount of K_2O (0.5–1.0%). A small amount of 0.25% of CuO was sufficient to increase the content of oxygenates. Among the catalysts of the first group, Cat. 302 (CuO, 0.5%) seemed to produce a maximum of oxygenates which attained to one half of the products (Fig. 5). Therefore it follows by no means that the products obtained with the catalysts of high activity are necessarily rich in the oxygenates. More oxygenates, however, were

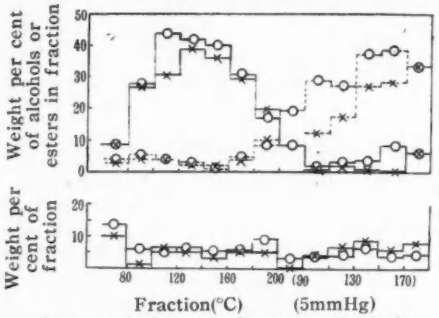
* CaO behaves similarly with K_2O in the physical and chemical adsorption of CO_2. (H. Uchida and T. Sato, ibid., 46, 103 (1951)).

8) P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.*, 59, 310 (1937).

9) S. Brunauer and P.H. Emmett, ibid., 62, 1732 (1940).

10) A. Juhola and E.O. Wiig, ibid., 71, 2078 (1949).

produced with Cat. 304 (Fig. 5). at lower reaction temperatures than at higher temperatures. The results may be interpreted to



Figs. 4–6 Above; Contents of alcohols and esters in oil products. Full line, alcohols; dotted line, esters.
Below; Weight per cent of fractions.
×; Cat. 101 ($2Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $1K_2O$)
(React. temperat., 180–230°C)
○; Cat. 301 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$)
(,, .. ,180–230°C)

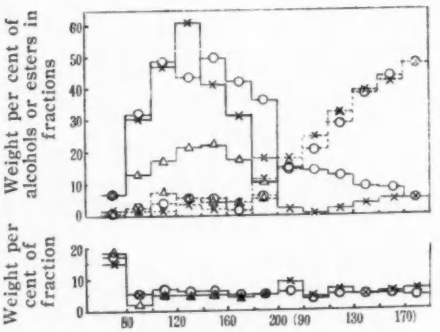


Fig. 5.
×; Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$) (180–230°C)
△; ,, (,,)
(240–250°C)
○; Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$) (170–250°C)

mean that in the case of a given catalyst, the lower the operation temperature is, the higher the yield in oxygenates is. The carbonyl compounds increased with the increasing amount of alcohols plus esters and amounted to an extent of from 4 to 7% in the fractions of between 100–200°C. Throughout the syntheses, with the catalysts of the first group, CO_2 in the exit gases remained small in amount at low operation temperatures and increased up to 40% with rising temperature. The higher temperature was favourable for the formation of gaseous olefins and methane, each attaining in amount to 2–3% and 7–9% respectively in the exit gas at 240–250°C. Aqueous products were usually about one half of the oily products in weight and contained 7–12% of alcohols*, and acids equivalent in amount to 2–2.7% acetic acid.

Among the catalysts of the second group, a particular catalyst (2.5 SiO_2, 2MgO, 1CaO, $1WO_3$, $1K_2O$) was active at low temperatures of 70–100°C.[6] A catalyst containing Al_2O_3 together with SiO_2, MgO, CaO, and K_2O (Cat. 330) was again highly active producing the oil at 30–50°C with 50% of the gas contraction (Fig. 3). The activity lasted only for 2 days, and the temperature of 170–180°C was required to maintain the contraction at 40% in the continued operation. With this catalyst, the product below 120°C contained very small amounts of alcohol (Fractions; 120–140°C, 4.4%, 140–160°C, 4.1%, 160–180°C, 6.0%), while that at higher temperatures (130–250°C) the somewhat greater amount (14.0%, 10.6%, 3.9%, of the respective fractions). The catalyst seemed rather less suitable for the alcohol synthesis than those of the first group. In this connection, H. Tramm[11] had already avoided a large quantity of diatomite earth in the precipitated iron catalyst for the alcohol synthesis. By the addition of CuO to Cat. 330 (Cat. 331), the activity was lowered (Fig. 3), while the somewhat higher yield of alcohols was obtained (Fig. 6), yet not very significantly. Similar behaviour was also found with the catalysts containing SiO_2, MgO, CaO, and K_2O with (Cat. 320) and without CuO (Cat. 209).

Among the precipitated iron catalysts, a catalyst promoted by MgO, CaO, CuO, and K_2O, but by neither Al_2O_3 nor SiO_2 was frequently used in the Fischer-Tropsch synthesis by H. Koelbel[12]. A fused catalyst of the similar promoter-composition (Cat. 311) was employed in the present experiment. It was found to be of a low activity, and produced a very small amount of oxygenates (Fig. 6) with a large quantity of high boiling fraction (Table I).

Microscopic Structure.—Large grains develop on the etched surface of Cat. 101 containing Al_2O_3, CaO, K_2O etc. and no CuO. The grains are divided into finer sub-grains by regular orientations of narrow grain boundaries (Photo. 1). These grains appeared as fine crystallites with sharp facets in the electron microscope (Photo. 2), their dimen-

* The water-soluble alcohols obtained with Cat. 301, comprised 0.4%-C_1, 7.0%-C_2, 1.2%-C_3, 0.4%-C_4.

11) H. Tramm, *Brennstoff Chem.*, **33**, 21 (1952).
12) H. Koelbel, and P. Ackermann et al., *Chem. Ing. Tech.*, **23**, 183 (1951).

TABLE I

PROMOTER-COMPOSITION AND FRACTION OF THE PRODUCT DISTILLED BELOW 200°C

Catalyst	101	301	302	303
Promoter-composition	$2Al_2O_3$, 1CaO $1WO_3$, 1MgO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO, $1K_2O$	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 1CuO, $0.5K_2O$
Fraction below 200°C wt. %	37.3	51.3	52.0	53.2 (180–230) 56.5 (240–250)
(Reaction temperature °C)	(180–230)	(180–250)	(170–250)	
Catalyst	304	311	209	210
Promoter-composition	$3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $0.25CuO$, $0.5K_2O$	3MgO, 1Cao, $1WO_3$, 1CuO, $1K_2O$	$2.5SiO_2$, 2MgO, 2CaO, $1K_2O$	$2.5SiO_2$, 2MgO, 2CaO, $1K_2O$, 0.5CuO
Fraction below 200°C wt. %	43.2 (180–230)	27.0	45.7	40.5
(Reaction temperature °C)	48.1 (235–250)	(180–270)	(180–250)	(180–250)
Catalyst	330			
Promoter-composition	$3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, $2.5K_2O$			
Fraction below 200°C wt. %	67.8 (30–110)			
(Reaction temperature °C)	47.0 (130–250)			

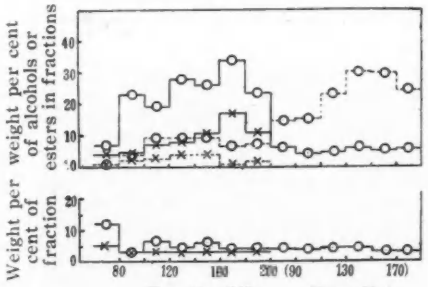


Fig. 6.
×; Cat. 311 (3MgO, 1CaO, $1WO_3$, 1CuO, $1K_2O$) (180–270°C)
○; Cat. 331 ($3Al_2O_3$, $2SiO_2$, 1CaO, 1MgO, 1CuO, $2K_2O$) (150–250°C)

sions being a few microns in the smallest. By the addition of a small amount of CuO (0.25%), the narrow grain boundaries disappeared (Photo. 3, 4). Increasing amounts of CuO caused the gradual appearance of intergranular inclusions (Photo. 5), which revealed the metallic lustre of copper before the etching (Cat. 303). Copper added in excess of the quantity which permitted the copper to dissolve into the grains, thus segregated along the grain boundaries. Quite different from those of the first group were the catalysts of the second group, containing glassy inclusions between the grains as previously reported[13,14] (Photo. 7), and not possessing well-developed cleavage surfaces (Photo. 8). This is a significant feature of the catalyst of the second group. The addition of copper gave no remarkable change in the microscopic structures of these catalysts. After the reduction in hydrogen, cracks wider than those of the catalysts of the first group appeared, probably because of stronger shrinkage of the grains. Cat. 330 which contained SiO_2 and Al_2O_3 with a large amount of K_2O, showed the regular orientations of narrower boundaries as well as the crystalline inclusions (Photo. 9 and 10).

Determination of Surface Properties of the Catalyst.—The results are summarised in Table II. The addition of copper seemed to bring about increase in the surface area. With respect to the surface concentration of K_2O, the data were not sufficient to give any definite effect of copper. The adsorption of CO by copper might prevent the S. Brunauer's[9] procedure for the estimation of the surface concentration of iron from the direct use of the method for the catalysts containing copper. Preliminary measurements of adsorption of CO at −78°C were, therefore, carried out with copper supported on Al_2O_3. Nearly the same amount of CO

13) Z.W. Wilchinsky, *Anal. Chem.*, **21**, 1188 (1949).
14) H. Uchida, N. Todo et al., *Rep. Chem. Ind. Res. Inst. Tokyo*, **46**, 11 (1951) (in Japanese).

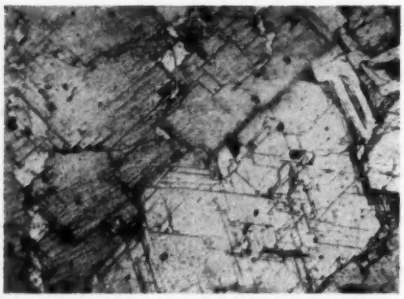


Photo. 1. Cat. 101 ($2Al_2O_3$, 1CaO, 1MgO, $1WO_3$, $1K_2O$) ×100

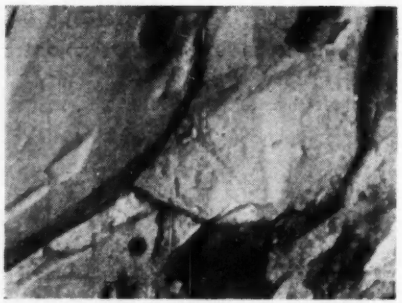


Photo. 2. Cat. 101 Replica ×5.000

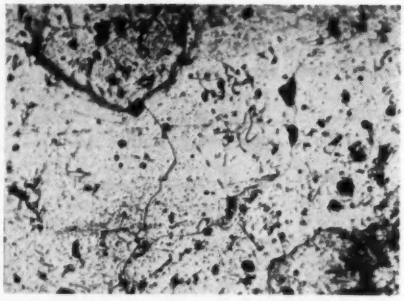


Photo. 3. Cat. 304 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.25CuO, $0.5K_2O$)

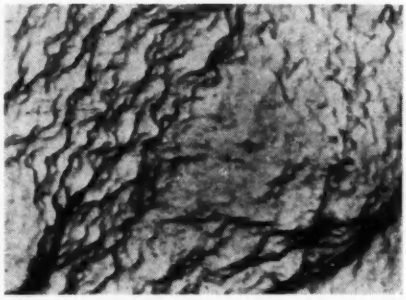


Photo. 4. Cat. 304 Replica

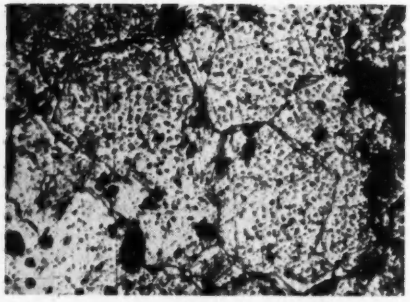


Photo. 5. Cat. 302 ($3Al_2O_3$, 1CaO, 1MgO, $1WO_3$, 0.5CuO $1K_2O$)

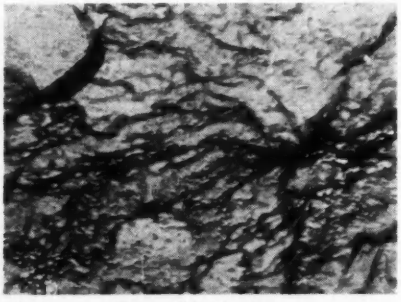


Photo. 6. Cat. 302 Replica

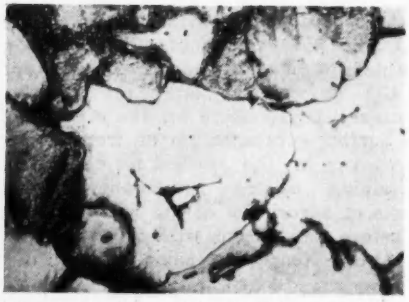


Photo. 7. Cat. 209 ($2.5SiO_2$, 2MgO, 2CaO, $1K_2O$)

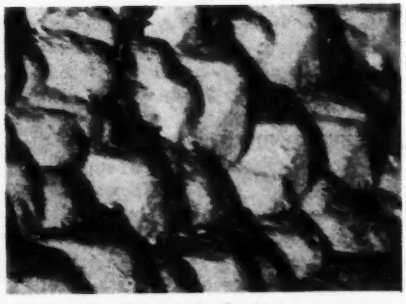


Photo. 8. Cat. 209 Replica

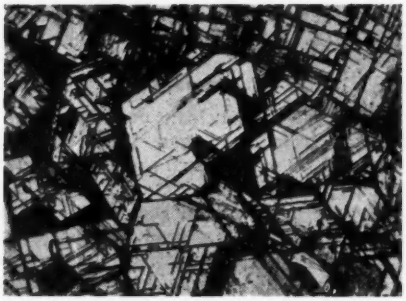


Photo. 9. Cat. 330 ($3Al_2O_3$, $2SiO_2$, ICaO, 1MgO, $2.5K_2O$) ×100

Photo. 10. Cat. 330 Replica ×5.000

was adsorbed at the following successive adsorptions; the one immediately after a degassing at 500°C and the one succeeding after an evacuation at 0°C for one hour (8.2 cc./g.Cu at the first and 7.9 cc./g.Cu at the second at 50 mm Hg). In contrast to the above, the major part of CO adsorbed at −78°C remained adsorbed through the evacuation at 0°C with Cat. 101. The difference between the first and the second measurements ($V_{CO} - V'_{CO}$) might be assumed, for convenience, to represent the surface concentration of iron with respect to the catalysts containing copper. The values of ($V_{CO} - V'_{CO}$) for the catalysts of the second group (Cat. 209, 320) were smaller than those for the first group, while the values of V_{CO} per unit area for the former were larger than those of the latter. The values of 1-A in Table II might express the surface concentration of the promoters, as of Al_2O_3, Cu, exclusive of both iron and K_2O (+CaO). In the case of the catalysts of the first group (with an exception of Cat. 302), the values increased with the addition of copper. This fact suggested that copper might concentrate on the surface.

Discussion

According to the study by H. Koelbel,[12] the addition of 0.05% of copper to iron caused a complete activation during the induction (or the formation) of the precipitated catalysts as well as a marked change in character of the products. On the other hand, according to S. Kodama,[15] 25% of copper to iron was needed for a sufficiently high yield of the oil. The present experiments have shown that a small amount of CuO was enough to bring about a considerable increase of the oxygenates. The microscopic structure, the surface area, and the chemisorption of CO changed also appreciably at the addition of this amount. These results were more like those of H. Koelbel. Since an excess addition of copper causes the segregation along the grain boundaries, it may be right that the further tendency for alcohols to increase considerably, should not be predicted.

Table II

Surface properties

Catalyst	101	301	302	303	304	311	209	210	330
Surface area $m^2/g.$	3.3	8.9	7.5	12.5	13.5	1.6	4.3	3.7	6.0
V_{eCO_2}/V_{mCO_2}	0.59	0.32	0.61	0.36	0.37	0.57	0.45	0.28	0.74
Pore volume cc./g.	0.120	0.112	0.122	0.112	0.124	0.123	0.136	0.102	0.138
Average pore radius Å	1385	465	600	355	325	2710	1100	1215	720
V_{CO} (at −78°C)	0.29	0.69	0.61	1.09	0.88		0.63	0.55	0.53
V'_{CO} (at −78°C)	0.096	0.24	0.24	0.39	0.36		0.43	0.28	0.12
1-A*	0.13	0.45	0.16	0.39	0.45		0.24	0.38	0.04

* $A = (V_{CO} - V'_{CO} + V_{eCO_2})/V_{mCO_2}$, V_{mCO_2}; volume of CO_2 forming the monolayer on the surface, V_{eCO_2}; volume of CO_2 chemisorbed at −78°C.

In the case of the precipitated iron catalysts for the hydrocarbon synthesis, the promoting action of copper was ascribed by H. Koelbel[12] to an easier formation of iron-carbon com-

15) S. Kodama, and H. Tawara et al., *J. Chem. Soc. Japan, (Ind. Sec.)* **45**, 1268 (1942) (in Japanese).

pounds. In this connection, S. Kodama[16] attributed it to an increase in number of the active centers at which iron carbides were formed. D. Gall,[17] and E. J. Gibson[18] assumed the synthesis mechanism to involve step-wise addition of methylene radicals to one end of a growing chain terminated by a hydroxymethylene radical or methylene radical to produce alcohols or alcohols and olefins as the initial, desorbed products. Therefore, primarily, the surface structures which may increase or favour the survival of hydroxymethylene radicals, and secondarily, those on which alcohols are not easily adsorbed to be converted to hydrocarbons, may be expected to increase the yield in alcohols. Since the alcohols have been shown to be increased by copper on the surface, copper may contribute to an easier formation of these structures. The structures might be ascribed to the carbides of iron, so far as the considerations by H. Koelbel and by S. Kodama were adopted. The assumption may be also consistent with the fact that the products obtained with Cat. 330 at low temperatures contain an extremely small amount of alcohols, while rather more abundant alcohol has been produced with increasing temperatures in the additional continued operation, during which the formation of the carbides may be achieved.

The low activity of Cat. 311 containing neither Al_2O_3 nor SiO_2 is expected, to a certain extent, due to its extremely small surface area. Since the catalyst has produced a large amount of high molecular fraction, Al_2O_3 together with SiO_2 are also effective in the shortening of carbon chains. On the other hand, Al_2O_3 and SiO_2 showed the promoting actions different from each other in the synthesis. Their microscopic structure as well as their behaviour for the chemisorption of CO differed also greatly between Al_2O_3 and SiO_2. Consequently, some structural difference of the surface may be supposed between the catalysts promoted by either Al_2O_3 or SiO_2.

16) S. Kodama, and S. Matsumura et al., ibid., **47**, 3 (1944).
17) D. Gall, and E.J. Gibson et al., *J. Appl. Chem.*, 2, 371 (1952).
18) E.J. Gibson and C.C. Gall, ibid., **4**, 49 (1954).

Summary

Among the fused iron catalysts for the syntheses from water-gas, those containing Al_2O_3 and K_2O as principal promoters behaved differently from those containing SiO_2, MgO, and K_2O as such. With the former, it was well known that the products rich in oxygenates were obtained when the synthesis could be carried out at low temperatures. In the present study, an addition of copper has proved to bring about an increase in oxygenates with a simultaneous decrease of the activity. A marked effect of copper on the yield of alcohols has already been realized at the addition of 0.25% of CuO into the catalyst, while no further remarkable effect has been easily observed with its increasing amounts. The observations of microscopic structures, such as the area, the chemisorption of CO_2, and CO showed also considerable changes at this amount of addition. An excess amount of copper is liable to segregate along the grain boundaries and hence seems to contribute little for the promotion.

By the addition of Al_2O_3 together with SiO_2 besides the usual promoters such as CaO, K_2O etc., a catalyst of the high activity, though of short durability, was obtained. In the product obtained with this catalyst at low temperatures, oxygenates have been extremely small, while those obtained by the additional operation at higher temperature are greater in amount.

A particular promoting action, quite different from that of Al_2O_3, has been ascribed to SiO_2.

Acknowledgment

The authors' thanks are due to Mr. Tadasuke Hosoya for his cooperation. He has been carrying out a part of this experiment.

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Raman Spectrum of Tropolone

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(Received August 18, 1954)

Introduction

Infra-red absorption of tropolone (cycloheptatrienolone) has been reported by several authors,[1,2,3] while its Raman data are not published yet. Just as with any other compound these two sets of information are indispensably needed in attempting to analyze and interpret the vibrational structure in the near ultra-violet absorption spectrum of tropolone vapor, which we also are investigating. In this paper are reported the results of our observation on the Raman spectrum of tropolone, one of the prototypes of seven-membered ring hydrocarbons.

Experimental

The spectrograph used is one constructed in this laboratory having three dense flint glass prisms of side lengths 6 cm. or more, and heights 4.5 cm. or more. The camera lens is a photographic objective of 21 cm. focal length and $F/2.6$ relative aperture, while the collimator lens is an achromat of 45 cm. focus and $F/5$ relative aperture. The spectrum is photographed on a strongly curved film strip placed at the focal surface of the instrument. The reciprocal dispersion of this spectrograph in the vicinity of Hg 4359 Å line is 39 Å per mm.

The scatterer was a solution of 5 g. tropolone in white crystalline powder form prepared in Prof. Nozoe's laboratory at Tohoku University, Sendai, dissolved in pure benzene, the concentration being about 1.6 mol. per litre. The solution was put into a Wood's tube of 1 cm. bore and 15 cm. length, and was irradiated sidewise with two glass mercury lamps, each consuming about 10 amp. current. Kodak "Super XX" panchromatic film was used and the time of exposure was 10 hr. For the calibration of wave-lengths iron arc spectrum was photographed in juxtaposition on the scattered spectrum.

Nine Raman scattered lines in all were observed, all being excited by the Hg 4359 Å and no line originating from the Hg 4047 Å was recorded. This is due to the strong absorption of tropolone lying in the region expected for the appearance of the latter lines. The measured wave-number shifts of the nine Raman lines are given in the 1st. column of Table I, along with their estimated intensities in brackets, the highest of which is assigned to grade number 5.

The tropolone solution was colorless at the start of the exposure, but soon began to turn yellow on irradiation, and the whole sample ultimately became a reddish-brown viscous fluid. This photochemical change accompanied by strong coloration made further continuation of the exposure almost meaningless, and a rather premature termination of the experiment was inevitable, although it was not favorable for satisfactorily recording weaker lines. The same photo-chemical coloration was experienced by us in photographing the vapor absorption spectrum of tropolone, but in that case the colored product remained in the liquid phase, not affecting the vapor phase absorption, provided pure tropolone still remained.

Discussion

Comparing our results with those of infra-red absorption reported by Shimanouchi et al., and given in the 2nd. column of our Table*, the agreement of wave-numbers is generally good, and the intensities go parallel. As we see in the Table three new low frequencies are found in Raman effect which were not measured in infra-red absorption, while counterparts of the two strong infra-red peaks at 1480 cm.$^{-1}$ and 1560 cm.$^{-1}$ could not be clearly confirmed on our film, owing to the approximate coincidence of positions of these lines with the strong scattered lines due to benzene.

In a Raman spectrum shifted lines with overtone or combination frequencies are not normally observed, so that our nine frequencies observed with not insignificant intensities, even under the unfavorable condition stated above, are to be considered all of fundamentals. From this standpoint the reported infra-red frequencies 770 cm.$^{-1}$, 880 cm.$^{-1}$, and 1050 cm.$^{-1}$ may very probably be interpreted as combinations and an overtone, $357+436$ cm.$^{-1}$, 2×436 cm.$^{-1}$, and $357+679$ cm.$^{-1}$, respectively, for which, naturally, Raman lines are not observed.

In the 3rd. column of the Table are given some of the fundamental vibration frequencies of tropolone in its electronically unexcited state, which are determined in the vibrational analysis of the near ultra-violet absorption bands of the vapor.[4] The agree-

* Shimanouchi et al. (ref. 3) have not reported the numerical value of frequencies and the intensities of the infra-red absorption peaks. The values given in our Table are those estimated from their published absorption curve.

1) Scott and Tarbell, *J. Am. Chem. Soc.*, **72**, 240 (1950).

2) Doering and Knox, *J. Am. Chem. Soc.*, **73**, 828 (1951).

3) K. Kuratani, M. Tuboi and T. Shimanouchi, This Bulletin **25**, 250 (1952).

4) MS. in preparation.

ment between these and the corresponding Raman values is very satisfactory. The largest discrepancy, 6 cm.$^{-1}$ between the 1262 cm.$^{-1}$ Raman and the 1256 cm.$^{-1}$ ultra-violet frequencies is probably due to change of bond forces concerned in the respective phases of aggregation, revealed specifically pronouncedly in this particular mode of vibration, even though the magnitude itself is quite small. In the near ultra-violet absorption spectrum we have found that the wave-number difference 643 cm.$^{-1}$ constitutes the key frequency, solely giving rise to many long band progressions, meaning that it is the excited state value of a totally symmetrical vibration frequency in the tropolone molecule with respect to its symmetry. In its spectral behaviour this frequency is entirely analogous to the 923 cm.$^{-1}$ excited state frequency of the benzene molecule. Now, the strong Raman shift 743 cm.$^{-1}$ in tropolone can plausibly be identified with the ground state value of the above 643 cm.$^{-1}$ Accordingly, we interpret 743 cm.$^{-1}$ as belonging to the totally symmetrical breathing vibration of the heptatriene ring, analogous to the 992 cm.$^{-1}$ frequency in benzene.

The three frequencies 1262, 1418 and 1610 cm.$^{-1}$, strongly observed in Raman and infra-red, and partly confirmed in ultra-violet absorption, may collectively be assigned to the stretching vibrations of the C—O bonds in the molecule. If these bonds were normal single and double bonds as a conventional non-resonating structure formula would indicate, their stretching vibration frequencies should be much more differentiated (1030 cm.$^{-1}$ in methanol and 1760 cm.$^{-1}$ in acetone). Then, the actual values of these frequencies, being concentrated in a comparatively narrow intermediate frequency region, suggest that the carbon-oxygen bonds in tropolone are of a somewhat different nature from either of the ordinary single or double bond. From electron diffraction measurements the two C—O distances are reported to be 1.34 Å and 1.26 Å,[5] values intermediate between Pauling's covalent radii sums 1.43 Å and 1.22 Å for the normal single and double C—O bonds. This may be understood as due mainly to the effect of resonance, and partly also to the influence of an intramolecular hydrogen bond bridging the two oxygen atoms in the molecule, an inference entirely compatible with the above-reported findings in the Raman spectrum.

By analogy to the benzen spectrum the frequencies 357, 436, 679, 743, 959 and 1208 cm.$^{-1}$ very probably belong to skeleton vibrations of the molecule, in which mainly the seven C atoms move. As we were not able to determine depolarization factors, the symmetry assignments of these fundamentals cannot be directly given now. However, we can at least see that the close parallelism thus found to exist between the skeleton vibration frequencies in benzene and tropolone simply reflects the close similarity of the ring forming valence forces, and hence of the electron structures of the two kinds of aromatic compounds.

The authors thank Professor T. Nozoe for the supply of samples of tropolone and related compounds.

TABLE I

VIBRATION FREQUENCIES IN TROPOLONE (cm.$^{-1}$)

Raman (present work) C_6H_6 solution	Infra-red absorption[3]** CS_2 and CCl_4 solutions	Ultra-violet absorption vapor
357 (2)		356
436 (1)		
679 (2)		678
743 (3)	735 (3)	741
	770 (2)	
	880 (2)	
	910 (1)	
959 (1)	950 (2)	
	1050 (2)	
1208 (2)	1200 (3)	
	1230 (4)	
1262 (4)	1260 (5)	1256
	1300 (4)	
1418 (5)	1415 (4)	
	1480 (4)	
	1560 (4)	
1610 (5)	1610 (4)	

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5) M. Kimura and M. Kubo, This Bulletin, **26**, 250 (1953).

** Regarding the frequency and intensity values for the infra-red absorption peaks see foot note * on p. 75.

Vat Dyes of Benzanthrone Series. XXIX.[1] *Chlorination of 16, 17-Dihydroxy-violanthrone with Phosphorus Pentachloride*

By Toshio MAKI and Mamoru MAEZAWA

(Received August 23, 1954)

A new attempt, a study of the reaction between 16, 17-dihydroxy-violanthrone(I) and phosphorus pentachloride, was carried out by us and certain new 16, 17-derivatives of violanthrone were obtained. They are highly interesting in the chemistry of this polynuclear system. A non aqueous colloidal suspension of 16,17-dihydroxy-violanthrone in *o*-dichlorobenzene was prepared and heated with an excess (2.5 times of the theory) of PCl_5 in a nitrogen atmosphere in order to prevent the oxidation of the two hydroxyls. The crude reaction product was a mixture of certain substances of distinctly different solubilities, which were very useful for the separation of the constituents with nitrobenzene and *o*-dichlorobenzene (see Table I).

TABLE I

SOLUBILITY RELATIONS

	Nitrobenzene		*o*-Dichlorobenzene	
Sbst.	210°	15°	180°	15°
(I)	Hardly sol.	Insol.	Practically insol.	Insol.
(II)-A,B	Insol.	Insol.	Insol.	Insol.
(III)-A,B	Sol.	Insol.	Hardly sol.	Insol.
(IV)	Sol.	Hardly sol.	Sol.	Hardly sol.
(V)	Sol.	Sol.	Sol.	Sol.

The presence of the hydroxyl in either or both of the 16,17-positions was conveniently detected by the sensitive color change of the cotton dyeings with acids and alkalis. We have found also that the absence of the hydroxyl is indicated by a water drop sensitiveness of the dyed fabrics, whereby a temporary reddish spot is produced by wetting with a water drop. Thus, for example, the initial 16,17-dihydroxy-violanthrone dyes cotton from a blue vat in clear yellowish green, which is quite indifferent against a water drop but becomes clear blue by dilute mineral acids and yellow green by dilute caustic alkalis (see Table II).

The part perfectly insoluble in boiling nitrobenzene is concluded as a monochloro-16,17-violanthrone-oxide (II-A of Table III), associated with a small amount of a dichloro compound (II-B). The 16,17-violanthrone-oxide is quite a new type of compound hitherto unknown in this series. The conlstitution is determined by us from the folowing facts: (1) Its blue violet color is entirely different from the yellowish green of the original 16,17-dihydroxy compound. The color change is remarkably hypsochromic. (2) It is extremely insoluble in organic solvents. Such insolubility is not found among the known blue-violet compounds of violanthrone series. (3) The hydroxyl group is absent. (4) It is sensitive to a water drop. (5) Its chlorine content is distinctly lower (found Cl, 8.68%) than that of the chlorine replacement of the 16,17-dihydroxyls to (IV) (calcd. Cl, 13.50%). (6) It is easily soluble

TABLE II

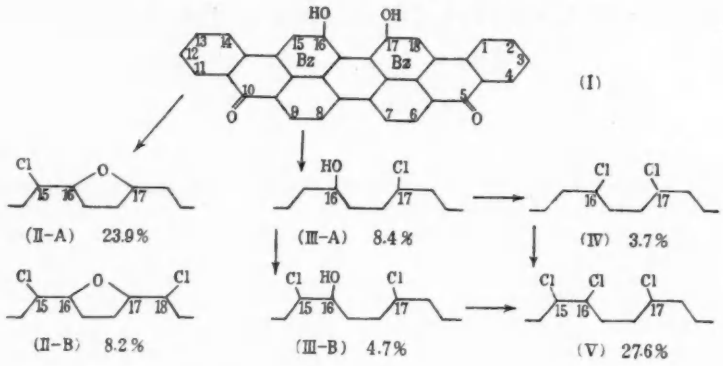
COLOR REACTIONS OF COTTON DYEINGS (1%)

Sbst.	Original shade	Dil. HCl	Dil.NaOH	Water drop	OH in 16.17-position
(I)	Yellowish green	Clear blue	Yellow green	Indifferent	2
(II)-A,B	Blue violet	Indifferent	Indifferent	Reddish	None
(III)-A,B	Greenish gray blue	Dark blue	Gray green	Almost indifferent	1
(IV)	Violet blue	Indifferent	Indifferent	Reddish	None
(V)	Grayish blue	Indifferent	Indifferent	Reddish	None

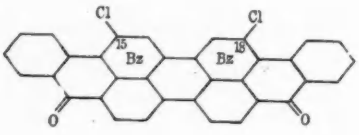
1) Read before the 6th Annual Meeting of the Chemical Society of Japan on April 5, 1953. Cf. the preceding report XXVIII, T. Maki, *J. Chem. Soc. Ind. Japan*, 50, 142 (1947).

TABLE III

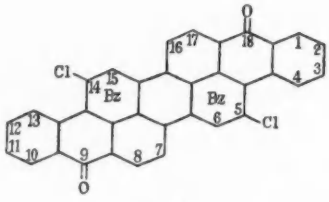
CONSTITUTION AND YIELD (% OF THE THEORY)



in alkaline hydrosulfite giving a blue vat, which proves the presence of the unchanged 5,10-dicarbonyls. (7) Considering the steric relation of 15-chloro or 15,18-dichloro group the monomolecular formula (II-A, B) is preferred by us rather than the bimolecular structure. The position of the chlorine atoms is most probably suggested as 15,18- for two reasons. One of the reasons is the ortho-orienting power of the hydroxyls and the other is our former studies on dichloro-violanthrone[2] and dichloro-isoviolanthrone[3]. Thus, when chlorination was carried out in organic solvents such as nitrobenzene, *o*-dichlorobenzene or acetic acid with free chlorine or sulfuryl chloride the chlorine atoms predominantly entered into 15,18-position



(VI)



(VII)

of violanthrone molecule giving a clear violet vat dye (VI), and also giving the equivalent 5,14-dichloro-isoviolanthrone (VII), which is the chief constituent of Indanthrene Brilliant Violet 2R and 4R.

Any traces of the starting material, 16,17-dihydroxy compound, were no longer found in the reaction product. The part soluble in boiling nitrobenzene but insoluble in hot *o*-dichlorobenzene is mainly 17-chloro-16-hydroxy-violanthrone (III-A), greenish gray blue dye, associated with 15,17-dichloro-16-hydroxy-violanthrone (III-B).

16,17-Dichloro-violanthrone (IV), a new, theoretically very important, violet blue substance, was obtained in minor quantity from the part soluble in hot *o*-dichlorobenzene by cooling. After chromatographic purification its yield was only 3.7% of the theory. The solubilities in organic solvents remarkably increased by the replacement of the 16,17-dihydroxyls with chlorine atoms. It is important that the color of 16,17-dichloro-violanthrone (IV) is found to be more bluish than that of violanthrone, while the 15,18-dichloro isomer (VI) is much redder than the latter.

Both 16,17-and 15,18-dichloro-violanthrone give dyeings of more clear shades than those of the mother substance, violanthrone. The part easily soluble in cold nitrobenzene and cold *o*-dichlorobenzene is mainly 15,16,17-trichloro-violanthrone (V), a grayish blue vat dye.

All the above substances (I—V), which are actually substituted in Bz-rings, have blue vats and Maki's discovery [2,3] on the relation between the blue vat and Bz-substitution in violanthrone derivatives was again confirmed.

2) T. Maki and T. Aoyama, *J. Chem. Soc. Ind. Japan, Suppl.*, 38, 636B (1935).
3) T. Maki and Y. Nagai, *Ber.*, 70, 1867 (1937).

Formerly, one of us studied the reaction between phosphorus pentachloride and 4,4'-dihydroxy-indanthrone, when the chief final product was 3,4,3',4'-tetrachloro-indanthrone[4] and 4,4'-dichloro compound was practically not obtained. It may be, therefore, a behaviour of PCl_5 that in the reactions with polynuclear anthraquinone derivatives nuclear chlorination predominates to a greater extent than the simple hydroxyl substitution. In the present case, also, trichloro-violanthrone (V) was obtained in comparatively higher yield.

The formation of the oxide ring (II-A,B), apparently by a dehydration of the two hydroxyls, is quite a special reaction between 16,17-dihydroxy-violanthrone and PCl_5. We tried to obtain a substance of the oxide type by fusing 1 part of 16,17-dihydroxy-violanthrone with 15 parts of anhydrous zinc chloride at 290°, but the result was negative. When a colloidal suspension of 1 mol. ratio of 16,17-dihydroxy-violanthrone in *o*-dichlorobenzene was boiled with 20 mol. ratio (large excess) of thionyl chloride for 12 hours the replacement of the hydroxyls with chlorine did not take place at all and only yellow green 15-chloro-16,17-dihydroxy-violanthrone (79%) was obtained together with some unchanged dihydroxy compound (21%).

Experimental Part

(1) Treatment of 16,17-Dihydroxy-violanthrone[5] with Phosphorus Pentachloride.—16,17-Dihydroxy-violanthrone (3.00 g.) was vatted with 24 g. of 25% sodium hydroxide, 5.0 g. of hydrosulfite conc. powder and 600 cc. of water by keeping at 55° for 20 minutes. The filtered vat was oxidized by a current of air and the collected precipitate, after thoroughly washed with water, was treated on the filter 3 times with methanol (20 cc., 10 cc. and 10 cc. resp.) in order to replace the water with methanol. The paste was then mixed with 150 g. of *o*-dichlorobenzene and the remaining methanol, together with about 1/3 the volume of the *o*-dichlorobenzene, was distilled off in a nitrogen atmosphere and thus a colloidal suspension of 16,17-dihydroxy-violanthrone in about 100 g. of *o*-dichlorobenzene was obtained. Phosphorus pentachloride (6.40 g., 5 mol. ratio) was added and also in a nitrogen atmosphere agitated 1 hour at room temperature, 4 hours on a boiling water bath and at last 1 hour at the boiling point of *o*-dichlorobenzene. After neutralizing with anhydrous sodium carbonate, the solvent was distilled off with steam and the collected precipitate, as a dry powder, was heated with 20 times of conc. sulfuric acid at 80° for 1 hour and then poured into water in order to hydrolyze the unstable chlorine such as $>CCl_2$ to $>C=O$. The weight of the reaction product was 3.17 g.

(2) The Part Insoluble in Boiling Nitrobenzene (II-A,B).—The crude reaction product (3.17 g.) was finely powdered and boiled with 317 g. of nitrobenzene under reflux and stirring for 1 hour and the insoluble (1.11 g.) was once more boiled with 111 g. of nitrobenzene. The yield of the final insoluble substance was 1.01 g. or 31.9% of the crude product. It is a violet black powder, entirely insoluble in boiling nitrobenzene and *o*-dichlorobenzene, soluble in conc. sulfuric acid with red violet color and dark reddish blue precipitate is formed by the addition of water. From a blue hydrosulfite vat (IN) it dyes cotton blue violet and the obtained dyeings are indifferent against acids and alkalis, but are sensitive to a water drop giving a temporary reddish spot, which disappears with the natural evaporation of water. Found: Cl, 8.68; calcd. for $C_{34}H_{13}O_3Cl$ (II-A): Cl, 7.02%; calcd. for $C_{34}H_{12}O_3Cl_2$ (II-B): Cl, 13.15%. So the substance corresponds mainly (73%) to 15-chloro-16,17-violanthrone oxide (II-A), associated with 27% of the dichloro oxide (II-B). The actual yield of (II-A) is therefore 23.9% and that of (II-B) is 8.2% of the theory.

(3) The Part Soluble in Boiling, but Insoluble in Cold Nitrobenzene.—By standing over night 0.76 g. and 0.05 g. of precipitates were obtained from the above first and second nitrobenzene filtrate respectively.

A) The Part Insoluble in Boiling *o*-Dichlorobenzene (III-A,B).—Both precipitates were combined (0.81 g. or 25.6% of the crude reaction product) and as a dry powder boiled with 81 g. of *o*-dichlorobenzene for 1 hour and the insoluble substance (0.50 g.) was once more boiled with 50 g. of the same solvent, whereby 0.41 g. (15% of the crude reaction product) of an insoluble matter was obtained. This is a violet black powder of dark blue streak and soluble in conc. sulfuric acid with red violet color. Hydrosulfite vat (IN) is blue with weak violet fluorescence and dyes cotton in greenish gray blue, which is changed by acids into dark blue and by alkalis into gray green, but is almost indifferent against a water drop. Found: Cl, 9.22, calcd. for $C_{34}H_{15}O_3Cl$ (III-A): Cl, 7.00%; calcd. for $C_{34}H_{14}O_3Cl_2$ (III-B): Cl, 13.10%. This substance is therefore composed of 64% of 17-chloro-16-hydroxy-violanthrone (III-A)

4) Dark violet needles from o-dichlorobenzene, in conc. sulfuric acid brown and with water blue violet precipitate. It was hardly soluble in alkaline hydrosulfite. T. Maki and T. Mine, *J. Chem. Soc. Ind. Japan*, 51, 15 (1948).

5) Benzanthrone (20 g.) was fused with 50 g. of KOH and 48.5 g. of isobutanol in presence of anhydr. sodium acetate (6 g.) at 110—2° for 3 hours. The crude product, as a dry powder, was boiled with 10 parts of *o*-dichlorobenzene to remove certain soluble impurities. The obtained 2, 2'-dibenzanthronyl was an olive gray powder, but of high purity, melting at 330—3° (corr.) and dissolving in conc. H_2SO_4 orange red without fluorescence. The yield was 15.8 g. (79.4% o. th.). Dibenzanthronyl (10 g.) was then dissolved in 300 g. of 84% H_2SO_4 and oxidized with 19 g. of 66% MnO_2 at 25—30° for 3 hours. The insoluble part was filtered through asbestos, thrown into water, and the obtained paste was heated with 15 g. of sodium bisulfite in 300 cc. of water and after acidification 16, 17-dihydroxy-violanthrone was collected. The yield was 8.0 g. (75.1% o. th.). The operations given in FIAT 1313, II, 83—5 should be somewhat modified.

and 36% of 15,17-dichloro-16-hydroxy compound (III-B). The actual yield of (III-A) is 8.4% and that of (III-B) is 4.7% of the theory.

B) The Part Soluble in Boiling, but Insoluble in Cold *o*-Dichlorobenzene (IV).—When the above *o*-dichlorobenzene filtrates (3A) were allowed to stand over night 0.27 g. (8% of the crude reaction product) of a violet black precipitate was obtained. In order to make it completely free from the trace of the associated chlorohydroxyl compounds (III-A,B) it was dissolved in 54 g. of boiling *o*-dichlorobenzene, chromatographed on alumina, developed with 32.4 g. of boiling nitrobenzene, washed with 10 cc. of alcohol and the upper dark blue gray layer was eluted 5 times with each 50 g. of boiling *o*-dichlorobenzene. After steam distillation of the solvent 0.12 g. (3.6% of the crude reaction product) of a purified substance was obtained, which is a violet black crystalline powder with metallic lustre. Found: Cl, 14.53%; calcd. for $C_{34}H_{14}O_2Cl_2$ (IV): Cl, 13.50%.

The hydrosulfite vat of this substance is blue with weak violet fluorescence and dyes cotton (IN) violet blue, more bluish than violanthrone and 15,18-dichloro-violanthrone (VI). Its dyeings are quite indifferent against acids and alkalis, but are sensitive to a water drop giving a temporary reddish spot. The substance has no connection with the hydroxyl group and corresponds to 16,17-dichloro-violanthrone (IV). Contrary to the hydroxylated compounds it is soluble in hot *o*-dichlorobenzene with intense violet blue color with strong red fluorescence. Conc. sulfuric acid solution is red violet without flourescence and blue precipitate is produced from the acid solution by water. The actual yield of 16,17-dichloro-violanthrone is about 3.7% of the theory.

(4) The Part Soluble in Cold Nitrobenzene and Cold *o*-Dichlorobenzene (V).—The above cold nitrobenzene filtrates (2) were combined (ca. 428 g.) and nearly 5/6 of this solvent was distilled off. After cooling 0.27 g. of an impure precipitate was removed and the clear filtrate was distilled with steam, when 0.89 g. of a violet black powder was obtained. Found: Cl, 19.72%; calcd. for $C_{34}H_{13}O_2Cl_3$ (V): Cl, 19.01%. It dyes cotton grayish blue from a blue hydrosulfite vat (IN) and the dyed fabrics are quite indifferent against acids and alkalis, but are sensitive to a water drop. The substance is found to be 15,16,17-trichloro-violanthrone (V), free from any hydroxyl groups. It is very easily soluble in *o*-dichlorobenzene in red violet color with strong red fluorescence and is soluble in conc. sulfuric acid red violet without fluorescence. A small quantity (0.06 g.) of the same substance was also obtained from the cold *o*-dichlorobenzene filtrates of (3B) after steam distillation of the solvent. The total yield of the trichloro-violanthrone (V) is therefore 0.95 g. or 27.6% of the theory.

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The Preparation of 4-Methoxy-2-butenal, a New Dienophile, and Notes on Related Compounds

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It is thought that the 2-butenals containing a functional substituent in the 4-position may be valuable as new type dienophiles for the practical use of the Diels-Alder reaction. No work on the synthesis of such γ-substituted crotonaldehydes had been found in the literature of the subject, till the formation of 4-dimethylamino-2-butenal was first reported by the authors,[1] who were unable to isolate the free aldehyde, but succeeded in isolating the 2,4-dinitrophenylhydrazone ethylsulfate. In this paper we wish to describe a synthesis of 4-methoxy-2-butenal, which was proved to be a dienophile, and to make several notes on new compounds obtained during the course of investigation on 4-dialkylamino- and 4-hydroxy-2-butenals.

Both attempts to prepare 4-bromo-2-butenal by hydrolysing its diacetate[2] (I) and to prepare 4-diethylamino-2-butenal by hydrolysing the diacetate (II), which had been derived from the bromo-compound through the action of diethylamine, were in vain. The two acetates cited here seemed to be extremely labile in the hydrolysis process.

$$BrCH_2CH:CHCH(OCOCH_3)_2 \longrightarrow$$
(I)
$$(C_2H_5)_2NCH_2CH:CHCH(OCOCH_3)_2$$
(II)

The second attempt to prepare amino-

1) I. Ichikizaki and Yao, the 6th annual meeting of the Chemical Society of Japan at Kyoto University on April 2, 1953.

2) H. Schmid and E. Crob, *Helv. Chim. Acta*, **32**, 77 (1949).

butenals was carried out by hydrolysing 4-dialkylamino-2-butenal diethyl acetals. 4-Dimethylamino-2-butynal diethyl acetal (III), prepared in a fairly good yield by the interaction of 3-dimethylamino-1-propynylmagnesium bromide and ethyl orthoformate in a benzene-ether solution, was hydrogenated to 4-diethylamino-2-butenal diethyl acetal (IV) in the presence of a catalyst such as palladium-barium sulfate. 4-Dimethylamino-2-butenal diethyl acetal (VI) was obtained from diethylpropargylamine via 4-dimethylamino-2-butynal diethyl acetal (V) through a similar process as above.

$$R_2NCH_2C{:}CMgBr \longrightarrow R_2NCH_2C{:}CCH(OC_2H_5)_2$$

(III) R=C_2H_5
(V) R=CH_3

$$\longrightarrow R_2NCH_2CH{:}CHCH(OC_2H_5)_2$$

(IV) R=C_2H_5
(VI) R=CH_3

These olefinic acetals were easily hydrolysed with mineral or organic acids, but repeated attempts to isolate the corresponding free aldehydes were all unsuccessful, because they were readily resinified on standing even for short times. Only when 4-dimethylamino-2-butenal diethyl acetal was hydrolysed with an equivalent amount of concentrated hydrochloric acid and immediately treated with Brady's reagent, the formation of 4-dimethylamino-2-butenal was confirmed by charachterizing it as the 2,4-dinitrophenylhydrazone ethylsulfate (VII).

$$\text{(VI)} \xrightarrow{\text{HCl, Brady reagent}} (CH_3)_2N^+HCH_2CH{:}CHCH{:}NNHC_6H_3(NO_2)_2\ C_2H_5SO_4^- \quad \text{(VII)}$$

Another investigation was made to prepare 4-hydroxy-2-butenal. By the action of ethyl orthoformate on propargyl alcohol dimagnesiumbromide, 4-hydroxy-2-butynal acetal (VIII) was obtained; however on catalytic reduction it did not yield 4-hydroxy-2-butenal acetal but a low-boiling oil which apparently contained 2-ethoxydihydrofurane (IX).[3]

$$BrMgOCH_2C{:}CMgBr \longrightarrow HOCH_2C{:}CCH(OC_2H_5)_2 \quad \text{(VIII)}$$

$$\longrightarrow CH_2CH{:}CHCHOC_2H_5 \quad \text{(IX)}$$
$$\quad\ \ |\!\!-\!\!O\!\!-\!\!|$$

The last attempt to prepare a free aldehyde of the class was made in a way to oxidize 4-methoxy-2-butenol to the corresponding aldehyde and resulted in success.

3) I.M. Heilbron, E.R.H. Jones and H.P. Koch, *J. Chem. Soc.*, (1942) 735.
Fernand Quennehen and Henn Normant, *Compt. rend.*, 228, 1301 (1949).

4-Methoxy-2-butynol (X) was prepared through a partial methylation of butynediol with dimethyl sulfate in an aqueous alkali, followed by a partial reduction to 4-methoxy-2-butenol (XI) in the presence of palladium-calcium carbonate in ethyl acetate. This was oxidized successfully according to either the method of Oppenauer[4] or that of Attenburrow et al.,[5] into 4-methoxy-2-butenal (XII) which was heated at 140°C with an equivalent amount of 2,3-dimethylbutadiene in a sealed tube to yield an adduct, 4,5-dimethyl-2-methoxymethyl-4-cyclohexene-1-carboxaldehyde (XIII).

$$(:CCH_2OH)_2 \longrightarrow CH_3OCH_2C{:}CCH_2OH \quad \text{(X)}$$

$$\longrightarrow CH_3OCH_2CH{:}CHCH_2OH \quad \text{(XI)}$$

$$\longrightarrow CH_3OCH_2CH{:}CHCHO \quad \text{(XII)}$$

$$CH_2{:}\overset{CH_3}{\overset{|}{C}}\!-\!\overset{CH_3}{\overset{|}{C}}{:}CH_2 \xrightarrow{CH_3\text{–}C\text{–}CH_2\text{–}CHCHO} CH_3\text{–}C\text{–}CH_2\text{–}CHCH_2OCH_3 \quad \text{(XIII)}$$

Experimental

4-Diethylamino-2-butenal Diacetate.—Diethylamine (3.2 g.) was dissolved in dry ether (25 cc.), and 4-bromo-2-butenal diacetate (5 g.) was added slowly with stirring and cooling. The mixture was allowed to stand over-night, then filtered. The filtrate was evaporated and the residue distilled to give 4-diethylamino-2-butenal diacetate (1.9 g.), a colorless oil, b.p. 108-109°/3 mm. On standing in air this became dark red. The iodomethylate, m.p. 125° (Found: N, 3.3%. $C_{13}H_{24}O_4NI$ requires 3.6%).

4-Diethylamino-2-butynal Diethyl Acetal and 4-Dimethylamino-2-butynal Diethyl Acetal.—After the most part of ether had been distilled off from an ethereal solution of ethylmagnesium bromide (from 2.5 g. of magnesium, 10.9 g. of ethyl bromide and 80 cc. of ether), dry benzene (100 cc.) was added. Then a solution of diethylpropargylamine[6] (11.1 g.) in benzene (10 cc.) was added dropwise with stirring. After the addition had been completed the solution was stirred for 30 minutes, and ethyl orthoformate (14.8 g.) was added. The reaction mixture thus obtained was heated to 65° and stirred vigorously for 3 hours, cooled and decomposed with a saturated solution of ammonium chloride. The organic layer was separated and the aqueous layer extracted with benzene. The combined extracts were washed, dried and distilled, giving 4-diethylamino-2-butynal diethyl acetal (10.5 g.), b.p. 90°/3.5 mm., $n_D^{16.5}$ 1.4492 (Found: N, 6.7%. $C_{12}H_{23}O_2N$ requires 6.5%).

Following a quite similar procedure, 4-dimethylamino-2-butynal diethyl acetal (10.5 g.) was pre-

4) A. Lauchenauer and H. Schins, *Helv. Chim. Acta*, 32, 1265 (1949).
5) J. Attenburrow, A.F.B. Cameron, I.H. Chapman, R.M. Evans, B.A. Hem, A.B.A. Jansen and T. Walker, *J. Chem. Soc.*, (1952) 1094.
6) John W. Copenhaver and Maurice H. Bigelow, "Acetylene and Carbon Monoxide Chemistry," (1949), p. 110.

pared by the action of ethyl orthoformate (18 g.) on 3-dimethylamino-1-propynylmagnesium bromide (from 2.6 g. of magnesium and 9 g. of dimethylpropargylamine[5]), b.p. 84-86°/6 mm., $n_D^{16.5}$ 1.4419. The iodomethylate, m.p. 139-140° (Found: N, 4.1%. $C_{11}H_{24}O_2NI$ requires 4.2%).

4-Diethylamino-2-butenal Diethyl Acetal and 4-Dimethylamino-2-butenal Diethyl Acetal.—4-Diethylamino-2-butynal diethyl acetal (15.6 g.) was dissolved in ethanol (25 cc.) and hydrogenated in the presence of 3% palladium-barium sulfate (0.5 g.). After 140 minutes one equivalent of hydrogen (1565 cc.) had been absorbed, the catalyst was then separated and the filtrate was distilled, giving 4-diethylamino-2-butenal diethyl acetal, b.p. 80-81°/4 mm., n_D^{15} 1.4402 (Found: N, 58.1%. $C_{12}H_{25}O_4N$ requires 58.2%). The iodomethylate, m.p. 130°.

4-Dimethylamino-2-butynal diethyl acetal was analogously hydrogenated (in 20 cc. of ethanol, 0.2 g. of the catalyst) to 4-dimethylamino-2-butenal diethyl acetal (4.0 g.), b. p. 62-62.5°/3 mm., n_D^{18} 1.4353. The iodomethylate, m.p. 115° (Found: N, 4.0%. $C_{11}H_{24}O_2NI$ requires 4.2%).

2,4-Dinitrophenylhydrazone Ethylsulfate of 4-Dimethylamino-2-butenal.—Concentrated hydrochloric acid (3 drops) was added to 4-dimethylamino-2-butenal diethyl acetal (0.1 g.). With an evolution of heat the mixture became dark red. Brady's reagent (3 cc.) was added to the solution. After 12 hours the reaction mixture was filtered, and the orange reddish needles were recrystallysed from alcohol, m.p. 185-186° (Found: C, 40.3%; H, 4.8%; N, 16.8%. $C_{14}H_{21}O_8N_5S$ requires C, 40.2%; H, 5.0%; N, 17.2%).

4-Hydroxy-2-butynal Diethyl Acetal.—An ethereal solution of ethylmagnesium bromide (from 15 g. of magnesium and 200 cc. of ether) was partly evaporated, 150 cc. of ether being removed. After benzene (200 cc.) had been added, a solution of propargyl alcohol[7] (12.5 g.) in benzene (120 cc.) was added dropwise to the mixture during 1 hour with stirring and heating on a water-bath. After a solution of ethyl orthoformate (49.5 g.) in benzene (50 cc.) had been added in small portions, stirring and heating were continued for 2 hours; then the reaction mixture was cooled and decomposed by adding a saturated aqueous solution of ammonium chloride. The organic layer was dried and fractionated to yield 4-hydroxy-2-butynal diethyl acetal (23.4 g.), b.p. 118-119°/3 mm. (Found: C, 59.8; H, 9.1%. $C_8H_{14}O_3$ requires C, 60.9; H, 8.8%).*

The acetal (18 g.) and a solution of tartaric acid (25 g. in 18 cc. of water) were agitated with a small amount of hydroquinone in an atmosphere of nitrogen, neutralized and then extracted with ether. A part of the extracts was treated with Brady's reagent to yield the 2,4-dinitrophenylhydrazone, orange needles from alcohol, m.p. 119° (Found: N, 27.5%. $C_{10}H_7O_8N_4$ requires 27.5%).

4-Methoxy-2-butynol.—Butynediol[8] (40 g.) was dissolved in an aqueous solution of sodium hydroxide (24 g. in 100 cc. of water). Dimethyl sulfate (31 g.) was added dropwise with agitating at the temperature not higher than 70°. After stirring had been continued at 80° for a further 2 hours, the reaction mixture was extracted continuously with ether over 12 hours. The extract was washed, dried and evaporated. The residue was fractionated cautiously to give dimethoxybutyne (4.1 g.), b.p. 54-55°/15 mm., and 4-methoxy-2-butynol (18.8 g.),[9] b. p. 96-97°/15 mm., 81-82°/5 mm., n_D^{20} 1.4593, d_4^{20} 1.0462 (Found: C, 58.0%; H, 8.2%. $C_5H_8O_2$ requires C, 59.9%; H, 8.0%).

4-Methoxy-2-butenol. — 4-Methoxy-2-butynol (28.9 g.) was hydrogenated, in ethyl acetate (30 cc.), in the presence of 3% palladium-calcium carbonate (2.5 g). One equivalent of hydrogen (7065 cc.) was absorbed within 5 hours. 4-Methoxy-2-butenol, b.p. 87-88°/20 mm., n_D^{20} 1.4485, d_4^{20} 0.9910 (Found: C, 58.3; H, 9.6%. $C_5H_{10}O_3$ requires C, 58.8; H, 9.9%).

4-Methoxy-2-butenol.—*A. By the Method of Attenburrow et. al.*—4-Methoxy-2-butenol (16.9 g.) was stirred for 30 minutes with a suspension of manganese dioxide (98.9 g.) in carbon tetrachloride (290 cc.). The mixture was filtered and evaporated at room temperature under a reduced pressure. The residue, with a small amount of hydroquinone, was distilled to give 4-methoxy-2-butenal (2.1 g.), a colorless oil with irritating odor, b.p. 72-75/26 mm. (Found: C, 59.5; H, 8.2%. $C_5H_8O_2$ requires C, 59.9; H, 8.0%). The 2,4-dinitrophenylhydrazone, m. p. 139-140° (Found: N, 19.8%. $C_{11}H_{12}N_2O_5$ requires 18.9%). The final residue (7.9 g.), an odorless oil, has not been investigated.

B. By the Method of Oppenauer (Modified).—Aluminium isopropoxide (9.9 g.) and 4-methoxy-2-butenol (15 g.) were heated gradually to 70-100° at 12 mm., the replaced isopropyl alcohol being distilled off through a Vigreux column (1.2×20 cm.). After 50 minutes, cinnamic aldehyde (23.9 g.) was added dropwise and the temperature of the oil-bath was kept at 130-150°. The distillate, b.p. 70-88° at 25-27 mm., amounted to 10.4 g. On rectification 4-methoxy-2-butenal (7.1 g.) was obtained. The analytical data was identical with that of the sample in A.

4,5-Dimethyl-2-methoxymethyl-4-cyclohexene-1-carboxaldehyde.—2,3-Dimethylbutadiene[10] (0.77 g.), 4-methoxy-2-butenal (0.61 g.) and petroleum ether (1 cc.) were heated at 140° in a sealed glass tube for 8 hours. The light yellow reaction mixture was fractionated to yield the adduct, a colorless oil with citral-like odor (0.66 g.), b.p. 82-84°/2.5 mm. (Found: C, 72.5%; H, 9.9. $C_{11}H_{18}O_2$ requires C, 72.1; H, 10.0%). The thiosemicarbazone, m.p. 152° (Found: C, 56.1;

7) ibid., p. 105.

* All the acetylenic compounds reported in this paper gave too low analytical values of carbon; these values were reproduced identically on repeated combustions. This analytical problem is serious, but has not been solved by the authors.

8) ibid., p. 98.

9) Hans J. Pistor, *Gem. Pantent*, 804, 569 (April 26, 1951).

10) Louis F. Fieser, "Experiments in Organic Chemistry," D.C. Health and Company, (1941), p. 383.

H, 8.2; N, 16.1%. $C_{12}H_{23}ON_3S$ requires C, 56.5; H, 8.2; N, 16.4%).

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Practical Method for Estimating Surface Tensions of Solutions

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Introduction

The surface tension of solutions has a great effect on the efficiency of gas-liquid contact in unit operations such as distillation, absorption and extraction, so it is desired to establish a simple and practical method for calculating the surface tension of solutions. Recently, Meissner and Michaels[1] presented a method of calculating surface tension of mixtures of organic liquids, which is based on the additivity of Sugden's parachor, but this method is not available for solutions composed of organic solute and a highly polar solvent such as water.

Prigogine and Marechal[2] and one of the present authors[3] developed independently a statistical mechanical theory of the surface tension of a solution of rod-like molecules and derived a relationship between the concentration of the solute in the surface layer and that in the bulk phase. Although the statistical mechanical method gives the most rigorous approach to the present problem, the expression for the surface tension obtained by this method takes a somewhat complicated form which is undesirable for practical purposes.

In this paper, we propose a simple semi-empirical method for calculating the surface tension of solutions, and this method is based on the assumption of the additivity of the parachor in the *surface layer*, not in the *bulk*, and is available for the solutions composed of liquids differing widely in polarity.

Additivity of Sugden's Parachor

Sugden's parachor, (P), can be practically written as follows:

$$(P)=V\cdot\gamma^{1/4}, \qquad (1)$$

where V is the molecular volume and γ is the surface tension of liquids. The parachor is independent of temperature and shows an additivity with respect to atoms or atomic groups constituting the molecule, in spite of a wide variety of intramolecular or intermolecular forces; the strength of the intermolecular force decreases, in general, with increasing temperature or with decreasing density, even in the same liquid. These facts suggest that the parachor will practically depend only on the atomic or molecular composition of the system. We may, therefore, write the parachor, (P), of the mixture of liquids A and B in the following form:

$$(P)=V\cdot\gamma^{1/4}=(1-x_b)(P)_A+x_b(P)_B, \qquad (2)$$

with

$$(P)_A=V_A\cdot\gamma_A^{1/4} \text{ and } (P)_B=V_B\cdot\gamma_B^{1/4}. \qquad (3)$$

Here $(P)_A$ and $(P)_B$ are the parachors, V_A and V_B the molecular volumes, and γ_A and γ_B the surface tensions of liquids A and B, respectively. x_b is the molar fraction of B in the bulk phase, and V is the mean molecular volume of the mixture. These relationships are essentially equivalent to those of Hammick and Andrew,[4] and of Meissner and Michaels.[1]

However in the case of the solutions showing an appreciable effect of adsorption such as aqueous solutions of organic substances, it seems to be more reasonable to assume the additivity of the parachor in the surface, for the parachor is essentially a quantity concerning the surface. The defect of M.-M.'s method mentioned already originates in the neglect of the effect of adsorption of the solute molecules on the surface, as has been pointed out by M. and M. themselves.[5]

According to the assumption mentioned above we obtain at once

1) H.P. Meissner and A.S. Michaels, *Ind. Eng. Chem.*, 41, 2782 (1949).

2) I. Prigogine and J. Marechal, *J. Colloid Sci.*, 7, 122 (1952).

3) M. Kurata, *Busseiron Kenkyu Researches on Chem. Phys.*, No. 58, 60 (1952), (in Japanese). This paper will be published in English in near future.

4) D.L. Hammick and L.W. Andrew, *J. Chem. Soc.*, (London) 1929, 754.

5) M.-M. proposed another empirical method for calculating the surface tension of aqueous solutions, but it is not adequate for practical purposes.

$$V_s \cdot \gamma^{1/4} = (1-x_s)(P)_A + x_s(P)_B, \quad (4)$$

instead of Eq. (2). Here V_s is the mean molecular volume and x_s the molar fraction of B, both in the surface layer. If the volume change on mixing is ignored, we can put

$$V_s = (1-x_s)V_A + x_s \cdot V_B. \quad (5)$$

Combining Eq. (4) with Eq. (5), and using the volume fraction of B-molecule in the surface, v_s, we obtain

$$\gamma = \{(1-v_s)\gamma_A^{1/4} + v_s \cdot \gamma_B^{1/4}\}^4. \quad (6)$$

This equation enables us to calculate the surface tension of the mixture in terms of the bulk concentration, x_b, provided that the relation of v_s to x_b is known.

Method for Calculating the Concentration of Solute in the Surface of a Solution

For the solutions of rod-like molecule B consisting of P segments, Prigogine[2] and one of the authors[3] derived statistically the following relation between the volume fraction of the solute molecule B in the bulk, v_b, and that in surface, v_s; i.e.

$$\{(1-v_b)^P \cdot v_s\}/\{(1-v_s)^P \cdot v_b\} = \exp\{P(\gamma_A - \gamma_B)/NkT\} \quad (7)$$

where N is the number of lattice points, or the number of the solvent molecule A, per unit area, k is the Boltzmann constant and T is the absolute temperature.

This relation can also be derived by considering a kind of chemical equilibrium between two states of the molecular arrangements; one of which is composed of P solvent molecules located in the surface layer and a solute molecule located in the bulk, and the other of which is composed of P solvent molecules in the bulk and a solute molecule in the surface, i.e.

$$P \cdot A_{surface} + B_{bulk} \rightleftarrows P \cdot A_{bulk} + B_{surface}. \quad (8)$$

The surface tension is the increase of the free energy per unit area due to shifting molecules from the bulk phase to the surface layer; then, γ_A/N or γ_B/N represents this increase of the free energy per molecule A or segment of B. As a molecule of B has P segments, $P(\gamma_B - \gamma_A)/N$ represents the increase of the free energy with the change in Eq. (8), from left to right, and we have for the equilibrium condition Eq. (7), which enables us to estimate the surface composition of the solution v_s in terms of v_b.[6]

Comparison with Experimental Data

If we denote by n_A and n_B the numbers of molecules per unit area of liquids A and B, respectively, the number of lattice points N is given by

$$N = n_A = Pn_B \quad (9)$$

according to the definition. Using this relation, we can write Eq. (7) as follows:

$$\log_{10}\left(\frac{1-v_s}{v_s}\right) + (P-1)\cdot\log_{10}(1-v_s) = \log_{10}\left(\frac{1-v_b}{v_b}\right) + (P-1)\cdot\log_{10}(1-v_b) + Q$$

with (10a)

$$Q \equiv \frac{P}{2.303\,kT}\left(\frac{\gamma_B}{Pn_B} - \frac{\gamma_A}{n_A}\right). \quad (10b)$$

In the estimation of Q, we adopt for n_A and n_B the values

$$n_A = (N/V_A)^{2/3} \text{ and } n_B = (N/V_B)^{2/3} \quad (11)$$

where N is the Avogadro number. For the value of P the following assumptions were made:

1) Aqueous solutions of fatty acids and alcohols,

P=Carbon Number. (12a)

2) Aqueous solutions of ketones,[7]

P=(Carbon Number)−1. (12b)

3) Aqueous solutions of halogen derivatives of fatty acids, e.g. homologue of monochloro acetic acid,

$$P = \begin{pmatrix}\text{Carbon}\\ \text{Number}\end{pmatrix}\cdot\left\{\begin{matrix}\text{Mol. Vol. of the Substance}\\ \text{Mol. Vol. of the Corresponding Fatty Acid}\end{matrix}\right\}. \quad (12c)$$

4) Solutions composed of organic solute

6) We assume in this paper that B molecules orientate parallel to the surface (the parallel type), then all of P segments of an adsorbed B molecule occupy the lattice points located in the surface layer. On the other hand, if B molecules do not orientate parallel to the surface (the vertical type), only one end-segment of an adsorbed B molecule occupies the lattice point located in the surface layer, and we obtain

$$\{(1-v_b)\cdot v_s\}/\{(1-v_s)\cdot v_b\} = \exp\{(\gamma_A - \gamma_B)/NkT\} \quad (7')$$

instead of Eq. (7). When $(\gamma_A - \gamma_B)$ is so large in comparison with NkT that v_s becomes much larger than v_b and the adsorption of B molecules contributes an appreciable effect on surface tension, we can safely ignore the adsorption of the vertical type in comparison with that of the parallel type at high dilutions. At high concentrations, both of the Eqs. (7) and (7') reduce to a common expression,

$$(1-v_b)/(1-v_s) = \exp\{(\gamma_A - \gamma_B)/NkT\} \quad (7'')$$

so we can again ignore the effect of the vertical type adsorption.

7) Cf. Ref. (1), p. 2787. M.-M. have pointed out that the ketones tend to affect the surface tension in a manner characteristic of the acid or alchol containing one less carbon atoms.

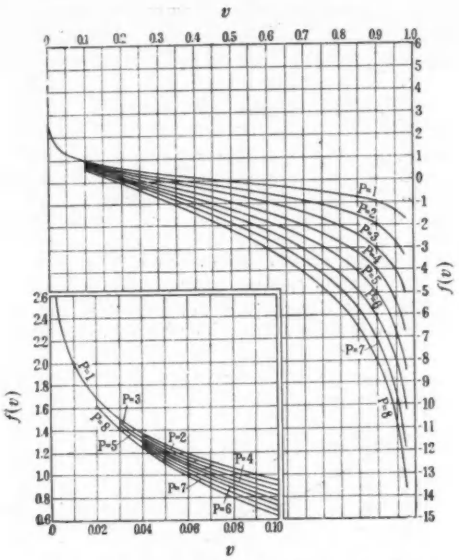


Fig. 1. Curves of $f(v)=\log_{10}(1-v)/v+(P-1)\times\log_{10}(1-v)$ vs. v for some value of P.

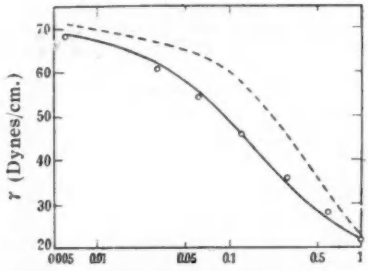


Fig. 2. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3OH at 30°C.
○ γ_{obs},
—— γ_{calc} (Present method),
- - - γ_{calc} (M.-M. method).

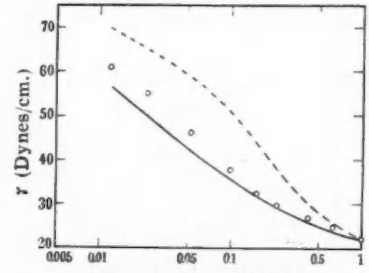


Fig. 3. Comparison between γ_{calc} and γ_{obs} of aqueous solution of C_2H_5OH at 25°C.

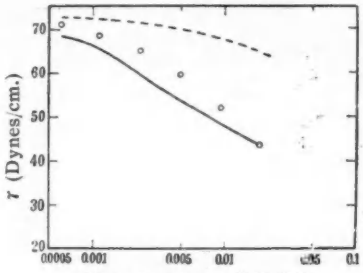


Fig. 4. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_3H_7OH at 15°C.

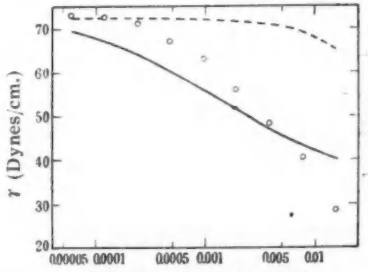


Fig. 5. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_4H_9OH at 15°C.

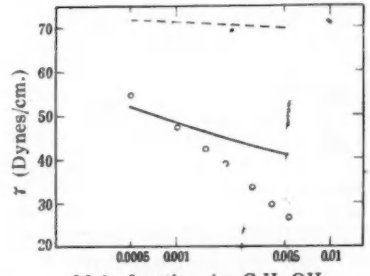


Fig. 6. Comparison between γ_{calc} and γ_{obs} of aqueous solution of iso-$C_5H_{11}OH$ at 30°C.

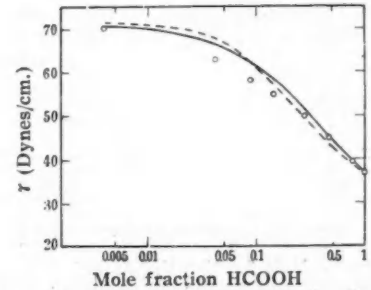
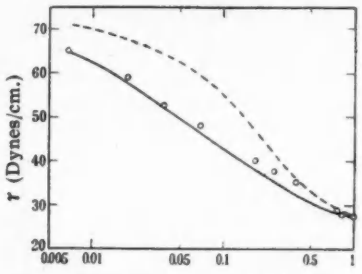
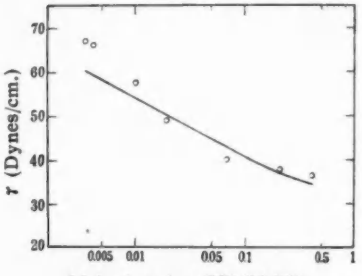


Fig. 7. Comparison between γ_{calc} and γ_{obs} of aqueous solution of HCOOH at 30°C.



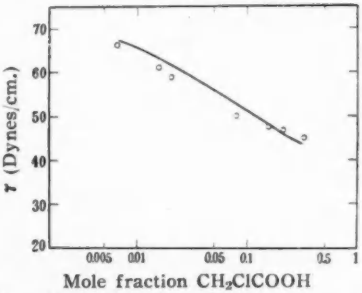
Mole fraction CH_3COOH

Fig. 8. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3COOH at 25°C.



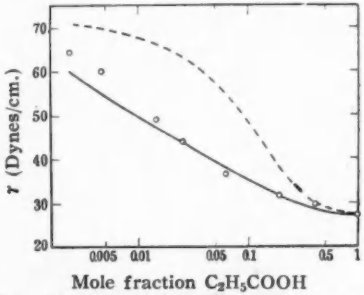
Mole fraction CCl_3COOH

Fig. 9. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CCl_3COOH at 25°C.



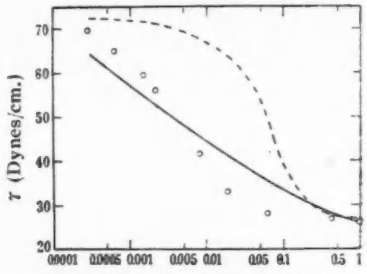
Mole fraction $CH_2ClCOOH$

Fig. 10. Comparison between γ_{calc} and γ_{obs} of aqueous solution of $CH_2ClCOOH$ at 25°C.



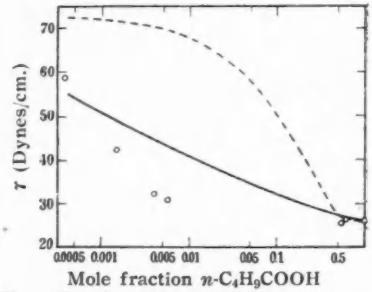
Mole fraction C_2H_5COOH

Fig. 11. Comparison between γ_{calc} and γ_{obs} of aqueous solution of C_2H_5COOH at 25°C.



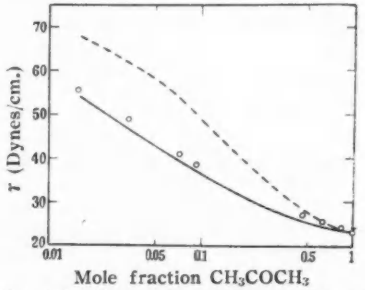
Mole fraction n-C_3H_7COOH

Fig. 12. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_3H_7COOH at 25°C.



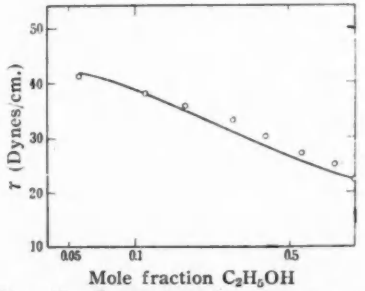
Mole fraction n-C_4H_9COOH

Fig. 13. Comparison between γ_{calc} and γ_{obs} of aqueous solution of n-C_4H_9COOH at 25°C.



Mole fraction CH_3COCH_3

Fig. 14. Comparison between γ_{calc} and γ_{obs} of aqueous solution of CH_3COCH_3 at 25°C.



Mole fraction C_2H_5OH

Fig. 15. Comparison between γ_{calc} and γ_{obs} of ethylene glycol solution of C_2H_5OH at 20°C.

and organic polar solvent,[8,9]

P=(Mol. Vol. of Solute)/(Mol. Vol. of Solvent) (12d)

The values of Q thus obtained are listed in Table I.

Fig. 1 shows the curves of $f(v)[\equiv\log_{10}\{(1-v)/v\}+(P-1)\cdot\log_{10}(1-v)]$vers. v for some values of P. Using this figure, we can easily solve Eq. (10a) graphically. For example, in the case of aqueous solution of CH_3OH at 30°C, P=1 and Q=−0.338 are obtained from

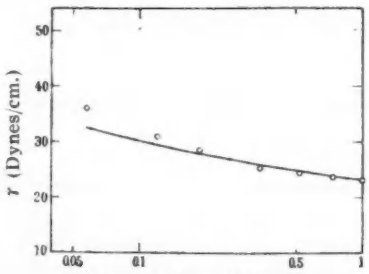


Fig. 16. Comparison between γ_{calc} and γ_{obs} of ethylene glycol solution of n-C_4H_9OH at 20°C.

TABLE I

LIST OF Q OF VARIOUS SYSTEMS

system A	system B	°C	Q
H_2O	CH_3OH	30	−0.338
H_2O	C_2H_5OH	25	−0.983
H_2O	n-C_3H_7OH	15	−1.662
H_2O	n-C_4H_9OH	20	−2.265
H_2O	i-$C_5H_{11}OH$	30	−2.801
H_2O	$HCOOH$	30	−0.111
H_2O	CH_3COOH	25	−0.857
H_2O	CCl_3COOH	25	−1.497
H_2O	$CHCl_2COOH$	25	−1.054
H_2O	$CH_2ClCOOH$	25	−0.758
H_2O	C_2H_5COOH	25	−1.532
H_2O	n-C_2H_7COOH	25	−2.157
H_2O	n-C_4H_9COOH	25	−2.801
H_2O	CH_3COCH_3	25	−0.868
CH_2OH | CH_2OH	C_2H_5OH	20	−0.549
CH_2OH | CH_2OH	n-C_4H_9OH	20	−1.396

8) For the sake of convenience we use

P=(Carbon Number of Solute)/(Carbon Number of Solvent) (12d′)

instead of Eq. (12d) in the calculations given below. The difference between two values of P obtained by Eqs. (12d) and (12d′) seems to be not appreciable in the examples adopted in this paper.

9) For mixtures of organic liquids, Meissner and Michaels' method can be used with sufficient accuracy, provided that the difference in the polarity of the liquids is not large.

TABLE II

COMPARISON BETWEEN γ_{calc} AND γ_{obs} OF AQUEOUS SOLUTION OF CH_3OH AT 30°C.

v_b	v_s	γ_{calc} (Dynes/cm.)	γ_{obs}
0.013	0.028	69.2	68.4
0.063	0.126	62.4	61.0
0.124	0.232	55.7	54.6
0.241	0.406	45.9	46.1
0.460	0.651	34.3	36.1
0.749	0.865	26.1	28.2

Eqs. (12a) and (10b). If v_b=0.241, we get $f(0.241)$=0.500, $f(v_s)=f(0.241)+Q$=0.162, and then v_s=0.406 from Fig. 1. The substitution of this value of v_s into Eq. (6) gives us γ= 45.9 dynes/cm, while the observed value of γ is 46.1 dynes/cm. v_s and γ_{calc} of this example are given in Table II with v_b and γ_{obs}.

The values of γ obtained by the present method, Eq. (6) with Eqs. (10) and (11), are shown in Figures 2 to 16 by solid lines,[10] where the observed values[11,12,13] are plotted by circles and also the calculated values of M.—M. are given by dotted lines for the sake of comparison. Although the agreement of the solid lines with observed data is not entirely excellent, the present method seems to be adequate for most practical purposes, if we take into consideration that the surface tention of the solution given here decreases extremely rapidly with increasing concentration of the solute. In the present method, the values necessary to calculate the surface tension are only four quantities, γ_A, γ_B, V_A and V_B.[14] γ_A and γ_B can be easily calculated, with good accuracy, by using the additivity of the atomic parachor; therefore we can use the present method even when the observed values of these two quantities are absent. This will be one of the merits of our method.

In the case of the mixtures of organic liquids, the difference between γ_A and γ_B are commonly small so that the effect of adsorption can be safely ignored, and then Eq. (2) or the method of M.—M. can be used with sufficient accuracy.

10) On performing calculation, we ignore the volume change on mixting; i.e.

$$V=(1-x_b)V_A+x_bV_B.$$

11) "International Critical Tables", Vol. 4, p. 467 (New York, McGraw-Hill Book Co., Inc., 1926).

12) H. Landolt and R. Börnstein, "Physikalisch-chemische Tabellen", 5th ed., (Berlin, J. Springer, 1928).

13) I. Yamakita and H. Aida, private communication.

14) When the pure solute is in solid state at the temperature in question (e.g. in the case of aqueous solution of CCl_3COOH), we can use the extrapolated values of γ_B and V_B from its liquid state.

Conclusion

We have presented a method for estimating the surface tension of the solutions composed of liquids differing widely in polarity, for which Meissner and Michael's method can not be applied, and have obtained good consistency of the calculated values with observed data. The percentage error, $\{(\gamma_{calc}-\gamma_{obs})/\gamma_{obs}\}\times 100$, is within 10% when $P<5$, and within 20% for large P.

In conclusion, the authors are indebted to Dr. I. Yamakita and Mr. H. Aida of Kyoto University for offering some unpublished data of the surface tension, and also to the Ministry of Education of the Japanese Government for a grant-in-aid.

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SHORT COMMUNICATIONS

Ultraviolet Spectrophotometric Determination of Iron with Ethylenediaminetetraacetic Acid

By Yasumitsu Uzumasa and Masakichi Nishimura

(Received September 6, 1954)

It was found that in acid medium ferric iron together with ethylenediaminetetraacetic acid (EDTA) develops an intense absorption in the ultraviolet region due to the formation of a complex which may be successfully utilized to a spectrophotometric determination of iron.

The procedure used in this study is as follows: an excess EDTA is added to a hydrochloric acid solution containing ferric iron, and the solution diluted to a definite volume. The resulting solution is 0.1N as to hydrochloric acid and 0.001M as to EDTA. The transmittancy measurements are made with a Beckman Model DU spectrophotometer equipped with 1 cm. silica cells, a blank of distilled water being referred to.

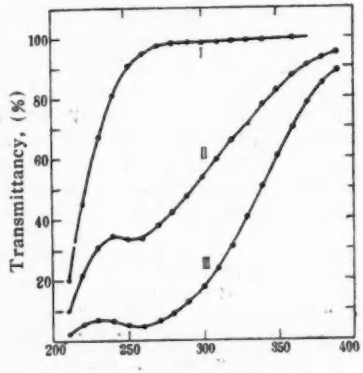

Fig. 1. Absorption spectra of ferric-ethylenediaminetetraacetic acid.
I: without iron, II: 5.0×10^{-4} M and III: 1.5×10^{-4} M ferric iron solution.

In Fig. 1, curve I shows the absorption spectrum of EDTA itself obtained by the said procedure; curves II and III represent the absorption spectra of ferric-EDTA complex solutions which contain 5×10^{-5} mol. and 1.5×10^{-4} mol. ferric iron per litre respectively. The latter solutions are characterized by a transmittancy minimum at 260 mμ.

Fig. 2 gives the calibration curve for iron at 260 mμ. The ferric-EDTA complex is stable and its molar absorbancy index at the absorption peak is somewhat larger than

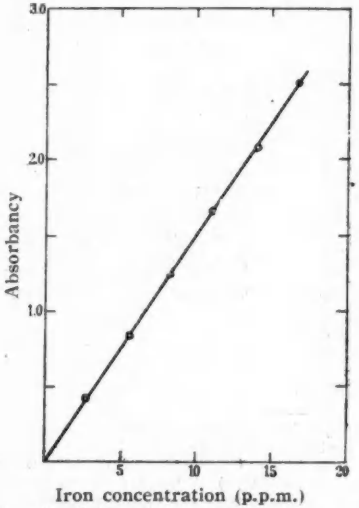

Fig. 2. Calibration curve for iron.

that of ferric-thiocyanate complex in the visible region.

The application of Job's continuous variations method reveals that one mole of ferric iron combines with one mole of EDTA.

Sulfuric acid as well as hydrochloric acid can be used in this determination, and the absorbancy remains constant over the range of 0.001 to 0.3N acid concentrations.

The work is being continued and its results will be reported in detail later.

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Separation of Sixth B Group Elements (S, Se, Te, Po) with Anion Exchange Resin

Yukiyoshi SASAKI

(Received September 27, 1954)

Selenium (IV), tellurium (IV) and polonium are known to form chloride complex anions of the type MCl_5^- or MCl_6^{--} in conc. hydrochloric acid solutions. This communication reports the complete separation of sulfur, selenium, tellurium and polonium by anion exchange chromatography of these chloride complexes.

The resin used was Dowex 1 X-4, porous strongly-basic type resin, ground less than 180 mesh, and was settled in a cylindrical bed 0.6 $cm^2 \times 3.8$ cm. Weighed quantities of 4 mg. of selenium, 6 mg. of tellurium and ca. $5 \times 10^{-3} \mu C$. of polonium were mixed and oxidized with fuming nitric acid. The mixture solution was evaporated to dryness, and dissolved in 1 cc. of 12 N hydrochloric acid. Besides them, the amount of 3 mg. of sulfur was added to the mixture in the form of sulfuric acid, as sulfur is volatile in its quadrivalent oxidation state in strong acidic solution.

The solution was placed at the top of the bed and the liquid level was allowed to fall to the resin, which was previously conditioned with 12 N hydrochloric acid. When the mixture solution was passing through the column, yellowish-green and yellow sharp adsorption bands due to selenium and tellurium respectively were clearly observed and distinguished from each other.

Elution was performed with 12 N hydrochloric acid at flow rate of about 0.2 cc./cm^2/min. at room temperature, and every 0.5 cc. fraction of effluent was collected and analyzed.

Sulfate was effectively not adsorbed to the resin and immediately appeared in the effluent, whereas the adsorption band of selenium moved only 1.5 cm. after the addition of 2.6 cc. of eluent (elution constant $E=0.3$),[1] and in the effluent the latter was not detected by the thiourea test.

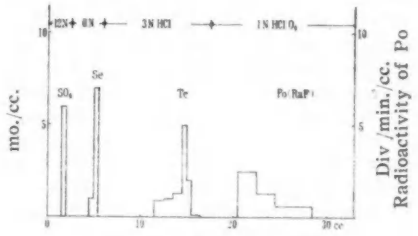

Fig. 1. Elution curve

Succeedingly, selenium was eluted completely with 3.5 cc. of 6 N hydrochloric acid, and then tellurium with 12 cc. of 2 N acid. Finally, polonium was desorbed with 1 N perchloric acid or 1N nitric acid.[2]

Sulfuric acid was determined as barium sulfate. Selenium and tellurium were reduced to their elementary states with sulfur dioxide and determined gravimetrically. Radioactivity of polonium was measured with the use of the Lauritsen electroscope. As shown in the figure, a nearly complete separation was obtained.

Within several hours after the adsorption of the sample, perchloric acid was effective to elute polonium. But after fifty hours, 3 N perchloric acid could elute only 10% of the total quantity of polonium; on the other hand, 3 N nitric acid was still effective. It was very likely that polonium was reduced in the bed or reacted irreversibly with ion exchange resin.

1) K.A. Kraus, G.E. Moore, *J. Am. Chem. Soc.*, **73**, 9 (1951), ibid., **75**, 1460 (1953).
2) T. Ishimori, : Abstracts of the Second Annual Meeting of The Japan Society for Analytical Chemistry, Oct. 1953 at Tokyo.

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Note on the Constancy of ϵ in the New Equation of State

By Tetsuya ISHIKAWA

(Received October 12, 1954)

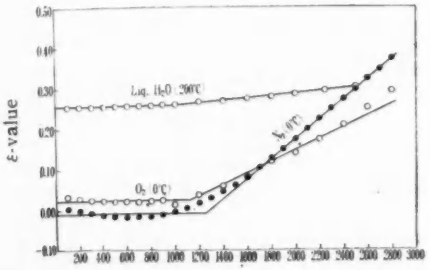
From the successive studies[1], I am convinced that in my equation of state, $(p+$

$a/V^{2-\varepsilon}(V-b)=RT$, $a=3p_cV_c^2$, $b=v_c/3$, which is valid for gases and liquids, an analytically determinable constant, ε, depends upon the molecular association, and isothermal ε values keep constant so far as the molecular association is little affected by applied pressures.

If the above conception of isothermal ε values is right, the change in molecular association, and hence the change in isothermal ε values at elevated pressures should go in the direction of increasing their values.

For water, as would be expected, isothermal ε values at 200°C for the critical temperature have been found to increase above 1000 bars, the manner of which is exemplified in Fig. 1 which shows ε - p(pressure) diagram at 200°C, the lowest temperature taken by Kennedy[2]. The constant range of ε is fairly good, and the change in ε at elevated pressures above 1000 bars is strictly linear up to his applied highest pressure, 2500 bars.

Similar phenomena are also observed for gaseous nitrogen and oxygen (see Fig. 1),



Pressure, bars for H_2O, atm. for N_2 atd O_2
Fig. 1. ε-p Diagrams for Livuid H_2O at 200°C and for N_2 and O_2 at 0°C.

which are the only two cases of being adoptable from International Critical Tables[3]. In these cases, however, the points which should belong to the constant range of ε are somewhat doubtful, and so it may be necessary to test percentage deviations of the calculated pressures from the observed pressures, 100 $(p_{calc.}-p_{obs.})/p_{obs.}$ (see Table I). As seem from Table I, the deviations are probably within the error limits, so that in these cases also the constant ranges of ε undoubtedly exist up to about 1000 atm., but the increasing rates of ε above 1000 atm. seem to be different from each other: for nitrogen the rate is linear at 1000 to 1600 atm. but strictly constant above 1600 up to 2800 atm., whereas for oxygen the rate is nearly constant at 1100 to 2400 atm.

The above analyses lead to the conclusion that isothermal ε values against pressures

TABLE I
PERCENTAGE DEVIATIONS FOR THE CONSTANT RANGE OF ε AT 0°C

	Nitrogen	Oxygen
	$b=30.03$	$b=24.81$
	log $a=5.911459$	log $a=5.916842$
	log V(0°C, 1 atm.) $=4.350323$	log V(0°C, 1 atm.) $=4.350134$
p(atm.)	% deviation	% deviation
100	+1.10	+1.27
200	+1.09	+1.14
300	+0.21	+0.53
400	−0.59	−0.34
500	−1.44	−0.68
600	−1.56	−0.83
700	−1.38	−0.99
800	−1.25	−0.71
900	−0.48	−0.31
1000	+0.63	+0.42
	mean 0.97	mean 0.72

are composed of two parts, the one being that of a constant range where no change in molecular association occurs at low to moderately high pressures, and the other being that of linear range, where molecular association is forced into a greater degree at elevated pressures above the limiting pressure which may be particular for a particular substance.

1) T. Ishikawa, This Bulletin, **26**, 78, 530 (1953), **27**, 226, 570 (1954); T. Ishikawa, M. Ikeda, ibid., **26**, 516 (1953).
2) G.C. Kennedy, *Amer. J. Sci.*, **248**, 540 (1950).
3) International Critical Tables, III, p. 8 for O_2, and p. 17 for N_2, both being the measurements by Amagat.

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Magnetic Resonance Absorption of Protons in Water Adsorbed on Carbon and Cellulose

By Kōji TANAKA and Kyōzō YAMAGATA

(Received December 4, 1954)

The line shapes of the proton magnetic resonance absorption in water adsorbed on carbon and cellulose was studied by an autodyne oscillator circuit[1]. We report here the derivatives of the absorption lines obtained with these substances at 20°C. The proton magnetic resonance absorption was observed by the variation of the resistance part of the oscillator coil, in which the sample was inserted. This phenomenon occurred as a resonance between the frequency of the oscillator and the transition frequency, a function of the static magnetic field ap-

plied to the sample. The derivatives of the absorption lines were recorded on photographic paper. The second moment was calculated from the curves of the recorded derivative and then the line width of the absorption curves was graphically determined.

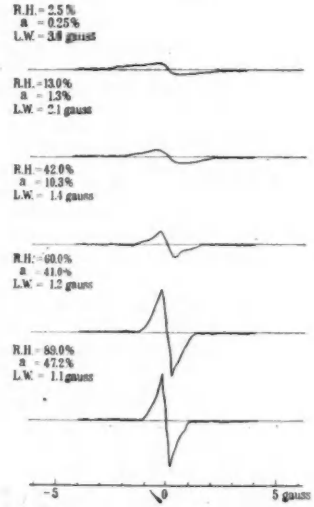

Fig. 1 Resonance line derivatives for carbon.
R.H. =Relative humidity (%)
a =Amount of adsorbed water vapor (%)
L.W. =Line width (gauss)

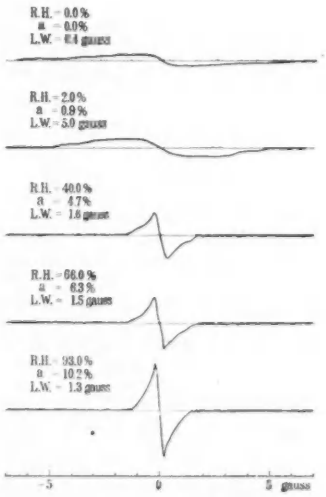

Fig. 2 Resonance line derivatives for cellulose.

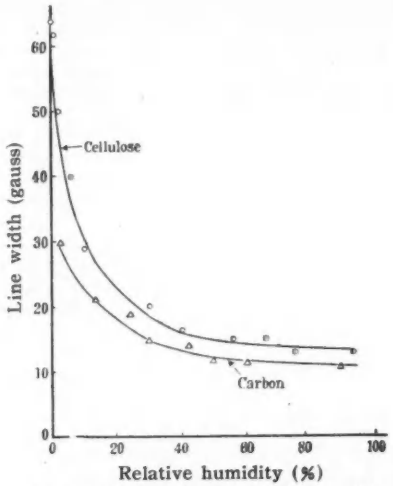

Fig. 3 The variation of line width of resonance absorption with relative humidity.

Carbon.—We used a vegetable active carbon (Takeda Co.) and freshly prepared conductivity water. The water vapor was adsorbed on the sample at 20°C for a period of 3 days in a desiccator of constant relative humidity. The curve of the magnetic resonance absorption of protons in water adsorbed on carbon at 20°C and the line width vs. relative humidity are shown in Fig. 1 and Fig. 3 respectively.

As shown in Fig. 1 the line shape becomes gradually sharp with the increase of relative humidity. In the higher relative humidity, the part of broad line shape practically disappears by the

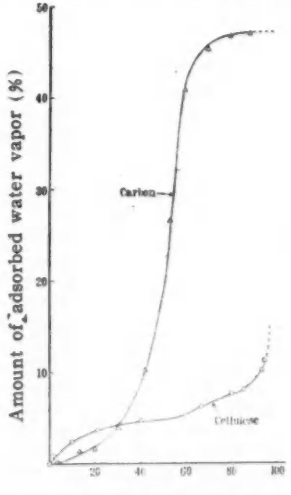

Fig. 4 Adsorption isotherms of water vapor on carbon and cellulose at 20°C.

influence of a large quantity of adsorbed water, although it should theoretically be observed.

The adsorption isotherm of water vapor on the active carbon measured at 20°C by spring balance method is shown in Fig. 4. By using the method of Brunauer, Emmett and Teller[2] it has been found that water is adsorbed on this sample with a mono-molecular layer, where the relative humidity is about 20%, so that we may conclude that the adsorbed water vapor of this monolayer is firmly held on the active carbon.

It is a remarkable fact that the line width (Fig. 3) rapidly decreases with the increase of relative humidity in the region of about 20% and that the sharp line shape (Fig. 1) overlaps gradually on the broad line shape. This is probably due to the considerable difference between the Brownian motion of protons in the water adsorbed in and above the mono-molecular layer. Thus it is demonstrated that the protons above the mono-molecular layer are movable, while the protons in the mono-molecular layer are rigid.

Cellulose.—A quantitative filter paper of best quality (Toyo Filter Paper No. 7) was used as cellulose material. Water vapor was adsorbed on the filter paper, previously dried in vacuo at 100°C, for a period of one day in a desiccator of constant relative humidity. In Figs. 2 and 3 are shown respectively the curves of the proton magnetic resonance absorption in water adsorbed on the cellulose at 20°C and the line width determined graphically vs. relative humidity.

The adsorption isotherm of water vapor on the filter paper measured at 20°C by spring balance method is of the usual sigmoid type as shown in Fig. 4. Resonance absorption of protons was found with cellulose even in the neighborhood of zero relative humidity, in contrast to carbon, and the line width was found to be about several gausses. This resonance absorption may be due to the protons in the cellulose molecule itself, but not to the adsorbed water. The line width both of cellulose and carbon decreases rapidly in the neighborhood of the relative humidity of 20%. When the relative humidity is above 40%, a sharper line shape appears in the case of cellulose, overlapping on the broad curve, and above 90% the line shape becomes strikingly sharp, quite in contrast to corbon. This is attributable to the known fact that the adsorption of water on cellulose suddenly increases in the neighborhood of saturated vapor pressure. It is a remarkable fact that the line shape of cellulose changes more rapidly than that of carbon, suggesting that the adsorption layer of water on cellulose has a character of a multiple layer, in contrast to that on the carbon.

The authors wish to express their appreciation to Professor M. Takeda and S. Kittaka for their interest in this work.

1) K. Sano, *Proc. J. Phys. Soc. Japan*, **6**, 228 (1951).
2) S. Brunauer, S.H. Emmett and E. Teller, *J. Am. Chem. Soc.*, **60**, 309 (1938); ibid., **62**, 1723(1940).

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